



217/782-6761

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Refer to: L1190400007/Madison Co.
Granite City/Taracorp
Superfund/Technical Reports

April 26, 1988

Stephen W. Holt
Senior Environmental Engineer
Environmental Control Department
NL Industries, Inc.
P.O. Box 1090
Highstown, NJ 08520

Dear Mr. Holt:

At our meeting on April 18, 1988, the IEPA agreed to provide NL with follow-up information. Attached are the analytical results of soil sampling by the Illinois Department of Public Health (IDPH) and several papers primarily concerning the uptake of metals by plants and potential effects on the food-chain.

Listed below are USEPA contact persons for data about lead carcinogenicity.

Carcinogen Assessment Group:

Dr. Robert Balials 202/382-5898

Environmental Criteria and Assessment Office:

Harlal Choudhrey 513/569-7536

The following reference provides information about the mean retention time for lead in the blood and soft tissues.

Handbook on the Toxicology of Metals, Volume II. Friberg, Lars; Nordberg, Grinnar F.; and Vouk, Velimir B. Editors Elsevier. 1986.

As discussed at the meeting, the IDPH has completed a Preliminary Health Assessment for the Taracorp site. The document is preliminary and has not been released to the public. The IDPH will, however, provide the report to NL in the next couple of weeks if no major deficiencies are revealed

through an internal review. The preliminary report does not include data which was generated by NL for the RI since the data was not available at the time of writing. NL's data will be incorporated into the revised report.

Should you require additional information, please contact me.

Sincerely,



Kenneth M. Miller, Project Manager
Federal Site Management Unit
Remedial Project Management Section
Division of Land Pollution Control

KMM:kls/3

cc: Terry Ayers, w/o att.
Author, w/att.
Connie Sullinger, w/o att.
Division File
Brad Bradley, w/att. ✓

ENVIRONMENTAL MISCELLANEOUS SAMPLE FORM

01691

1. NAME OF SOURCE: GRANITE CITY SAMPLE #1

2. ADDRESS:
STREET OR RR GRAND AVE
CITY, TOWN, STATE GRANITE CITY, ILL. ZIP CODE 62040 COUNTY: 1.19

3. DATE COLLECTED: 10-16-87 4. TIME COLLECTED: 1:40

5. TYPE OF SAMPLE: SOIL

6. COLLECTED BY: DAVID R. WEBB

OFFICIAL USE

9. MICROFILM NO.:

10. TRAN CODE: 35

11. REGION OR LHD:

12. LABORATORY ID: 001

13. COLLECTOR ID:

14. SAMPLE NUMBER:

7. SOURCE OF SAMPLE: OPEN LOT BETWEEN 15TH & 16TH STS
STREETS ON GRAND AVE

8. MAIL REPORT TO: DR. PH. REG. 104
STREET: C. T. HARRISON RD.
CITY/STATE: EDWARDSVILLE, ILL. ZIP CODE: 62225
TELEPHONE NUMBER: - -

ANALYSIS REQUESTED: CONCENTRATION OF ARSENIC, CADMIUM, CHROMIUM, LEAD, AND NICKEL IF POSSIBLE.

COMMENTS: SAMPLE IS A COMPOSITE FROM 3 DIFFERENT POINTS. SAMPLE IS FROM THE UPPER 2" OF SURFACE SOIL.
SAMPLE #1 OF 4 FROM AREA SURROUNDING TARMAC.

13. LABORATORY RESULTS:							
PARAMETER	ID	RESULT	UNIT	PARAMETER	ID	RESULT	UNIT
Arsenic in soil		16.9	mg/L	Lead in soil		1437.5	mg/L
Cadmium in soil		2.2	mg/L				
Chromium in soil		18.57	mg/L				
Nickel in soil		34.39	mg/L				

*CODE UNIT AS FOLLOWS:
% = PERCENT
A = GRAMS
B = /OIL

C = DECC
P = DECP
H = /100ML

I = MICROGRAM/L
J = /100 GML
L = MG/L

M = /ML
O = COLOR
T = TU

U = MICROGRAM/ML
X = PPM
Y = PPM

16. DATE RECEIVED AT LABORATORY: 11-11-87 17. DATE REPORTED FROM LABORATORY: 12-8-87

JAN 25 1988

ANALYST: JH, SH

REMARKS:

LHD STAMP

ENVIRONMENTAL MISCELLANEOUS SAMPLE FORM

1. NAME OF SOURCE: <u>GRANITE CITY SAMPLE #2</u>		OFFICIAL USE													
2. ADDRESS: STREET OR RR: <u>16TH STREET</u> CITY, TOWN, STATE: <u>GRANITE CITY</u> <u>IL</u> ZIP CODE: <u>62040</u> COUNTY: <u>119</u> (SEE BACK)		9. MICROFILM NBR: <u> </u> 10. TRAIL CODE: <u>35</u> 11. REGION OR LHD: <u>041</u> 12. LABORATORY ID: <u> </u> 13. COLLECTOR ID: <u> </u> 14. SAMPLE NUMBER: <u> </u>													
3. DATE COLLECTED: <u>10-16-87</u> 4. TIME COLLECTED: <u>1:50</u> 5. TYPE OF SAMPLE: <u>SOIL</u> 6. COLLECTED BY: <u>DAVID R. NEBB</u>		7. SOURCE OF SAMPLE: <u>OPEN AREA ON 16TH STREET BETWEEN DELMAR AND EDISON AVENUES</u> 8. MAIL REPORT TO: <u>DDPH-REGION 4</u> STREET: <u>COTTONWOOD RD.</u> CITY/STATE: <u>EDWARDSVILLE</u> <u>IL</u> ZIP CODE: <u>62025</u> TELEPHONE NUMBER: <u> </u> - <u> </u> - <u> </u>													
ANALYSIS REQUESTED: <u>CONCENTRATION OF ARSENIC, CADMIUM, CHROMIUM, LEAD, AND NICKEL</u>															
COMMENTS: <u>COMPOSITE SAMPLE FROM 3 DIFFERENT SAMPLING PRINTS TOP 2" OF SOIL</u> <u>SAMPLE #2 OF 4 SAMPLES TAKEN IN SITE VICINITY OF TARRACAP</u>															
<table border="1" style="width: 100%; border-collapse: collapse;"><thead><tr><th colspan="2">14. LABORATORY RESULTS:</th></tr><tr><th>PARAMETER</th><th>RESULT</th></tr></thead><tbody><tr><td>Arsenic in Soil</td><td>6.30 mg/g</td></tr><tr><td>Cadmium in Soil</td><td>9.99 mg/g</td></tr><tr><td>Chromium in Soil</td><td>33.74 mg/g</td></tr><tr><td>Nickel in Soil</td><td>35.18 mg/g</td></tr></tbody></table>				14. LABORATORY RESULTS:		PARAMETER	RESULT	Arsenic in Soil	6.30 mg/g	Cadmium in Soil	9.99 mg/g	Chromium in Soil	33.74 mg/g	Nickel in Soil	35.18 mg/g
14. LABORATORY RESULTS:															
PARAMETER	RESULT														
Arsenic in Soil	6.30 mg/g														
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B = / OZ.	L = MG./L.	T = TU	Y = PPM												
15. DATE RECEIVED AT LABORATORY: <u>10-16-87</u> <u>NOV 35 1987</u>		16. DATE REPORTED FROM LABORATORY: <u>2-8-88</u> ANALYST: <u>gri, f</u>													
REMARKS: 		LHD STAMP 													

ENVIRONMENTAL MISCELLANEOUS SAMPLE FORM

01684

1. NAME OF SOURCE: <u>GRANITE CITY SAMPLE #3</u>		OFFICIAL USE																																									
2. ADDRESS: STREET OR HWY: <u>20th STREET</u> CITY, TOWN, STATE: <u>GRANITE CITY</u> <u>IL</u> <u>62040</u> COUNTY: <u>119</u> <small>(SEE BACK)</small>		9. MICROFILM NO.: _____ 10. TRAIL CODE: <u>SS</u> 11. REGION OR LHD: _____ 12. LABORATORY ID: <u>021</u> 13. COLLECTOR ID: _____ 14. SAMPLE NUMBER: _____																																									
3. DATE COLLECTED: <u>10-14-87</u> 4. TIME COLLECTED: _____		5. MAIL REPORT TO:																																									
5. TYPE OF SAMPLE: <u>SOIL</u>		NAME: <u>EDPH-REGION 6</u>																																									
6. COLLECTED BY: <u>DAVID R WEBB</u>		STREET: <u>CARTONWOOD RD</u>																																									
7. SOURCE OF SAMPLE: <u>PARK BETWEEN 20th</u> <u>NIEDRINGHAUS, AND DELMAR</u>		CITY/STATE: <u>EDWARDSVILLE</u> <u>IL</u> <u>62225</u>																																									
8. MAIL REPORT TO:		ZIP CODE: <u>62225</u>																																									
9. ANALYSIS REQUESTED: <u>CONCENTRATION OF ARSENIC, CADMIUM, CHROMIUM, LEAD AND NICKEL.</u>		TELEPHONE NUMBER: _____																																									
COMMENTS: <u>COMPOSITE SAMPLE FROM 3 DIFFERENT SAMPLING POINTS.</u> <u>TOP 2" OF SOIL</u> <u>SAMPLE # 3 OF 4 SAMPLES TAKEN IN THE VICINITY OF TERRACORP.</u>																																											
14. LABORATORY RESULTS:																																											
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15. DATE RECEIVED AT LABORATORY: <u>10-14-87</u>		16. DATE REPORTED FROM LABORATORY: <u>10-20-87</u>																																									
REMARKS:		ANALYST: <u>JH</u> <u>PH</u>																																									
<div style="border: 1px solid black; height: 100px; width: 100%;"></div>		<div style="border: 1px solid black; height: 100px; width: 100%; text-align: center; padding-top: 50px;">LHD STAMP</div>																																									

ENVIRONMENTAL MISCELLANEOUS SAMPLE FORM

01682

1. NAME OF SOURCE: GRANITE CITY SAMPLE # 4

2. ADDRESS:

STREET OR RD. MADISON STREETCITY, TOWN, STATE GRANITE CITY 62040 COUNTY 1193. DATE COLLECTED: 10-10-88 4. TIME COLLECTED: 62105. TYPE OF SAMPLE: SOIL6. COLLECTED BY: DAVID R. WEBB

7. SOURCE OF SAMPLE:

PARK AT MADISON AND 23RD
ON EAST SIDE OF MADISON STREET

8. MAIL REPORT TO:

NAME: REGION 4STREET: CATHERWOOD RD.CITY/STATE: EDMUNDVILLETELEPHONE NUMBER: - -

OFFICIAL USE

9. MICROFILM NBR: 10. TRAN CODE: 5511. REGION OR LHD: 12. LABORATORY ID: 13. COLLECTOR ID: 14. SAMPLE NUMBER:

ANALYSIS REQUESTED:

CONCENTRATION OF ARSENIC, CADMIUM, CHROMIUM,
LEAD AND NICKEL.

COMMENTS:

COMPOSITE SAMPLE FROM 3 DIFFERENT SAMPLING POINTS
TOP 2" OF SOIL.SAMPLE # 4 OF 4 SAMPLES TAKEN IN THE VICINITY OF TARBORD

14. LABORATORY RESULTS:

PARAMETER	ID	RESULT	UNIT	PARAMETER	ID	RESULT	UNIT
Arsenic in Soil		7.89	mg/g	Pb in Soil		63.9	mg/g
Cadmium in Soil		6.40	mg/g				
Chromium in Soil		9.64	mg/g				
Nickel in soil		23.19	mg/g				

*CODE UNIT AS FOLLOWS:

P = PERCENT
A = GRAMS
B = /GM.C = DEGC
F = DEGF
H = /100MLI = MICROGRAM/L
J = /100 GM.
L = MG/LM = /ML
O = COLOR
T = TUU = MICROGM./ML
X = PPM
Y = PPB

15. DATE RECEIVED AT LABORATORY:

10-25-88

16. DATE REPORTED FROM LABORATORY:

10-25-88ANALYST:

REMARKS:

LHD STAMP

THE UPTAKE, DISTRIBUTION, AND EFFECT OF CADMIUM AND LEAD IN PLANTS

D. E. KOEPPE

Department of Agronomy, University of Illinois, Urbana, Ill. 61801 (U.S.A.)

(Received July 9th, 1976)

ABSTRACT

Lead and cadmium have been dispersed into the environment in increasing concentrations over the last century. In most instances this dispersal has been highly localized. This localization, along with reports of Pb and Cd toxicity to a variety of organisms in many food chains, amplifies the need for more knowledge about the uptake, distribution, and effects of these metals in primary producers.

Because both Pb and Cd are tightly bound to both organic and inorganic surfaces, their movement into and through plants is largely affected by environmental conditions surrounding the plants, as well as the physiological condition of the plants.

This paper reviews the uptake, translocation, and effect of Pb and Cd in corn, soybeans, and several other agronomic species. Cadmium is more toxic to both corn and soybeans than is Pb, and soybeans are more susceptible to both Cd and Pb than is corn. Binding and mobility properties are thought to be largely responsible for these differences.

INTRODUCTION

Lead and cadmium are dispersed into the environment from a variety of sources. Cadmium is generated from smelting industries, attrition of automobile tires, burning of diesel and heating oil¹⁵, phosphate fertilizers⁴, and from anaerobically digested sewage sludge²¹ which is disposed of on land. Lead is deposited near highways through the burning of leaded gasolines by automobiles and is also present in sewage sludge²⁰. In addition, Pb is disseminated from metal ore deposits, mining, smelting, certain industrial operations, or pesticide use². Thus, the potential exists in areas of high insult for effects of Pb and Cd on plants^{29-44, 49}, and subsequently in food chains. This paper con-

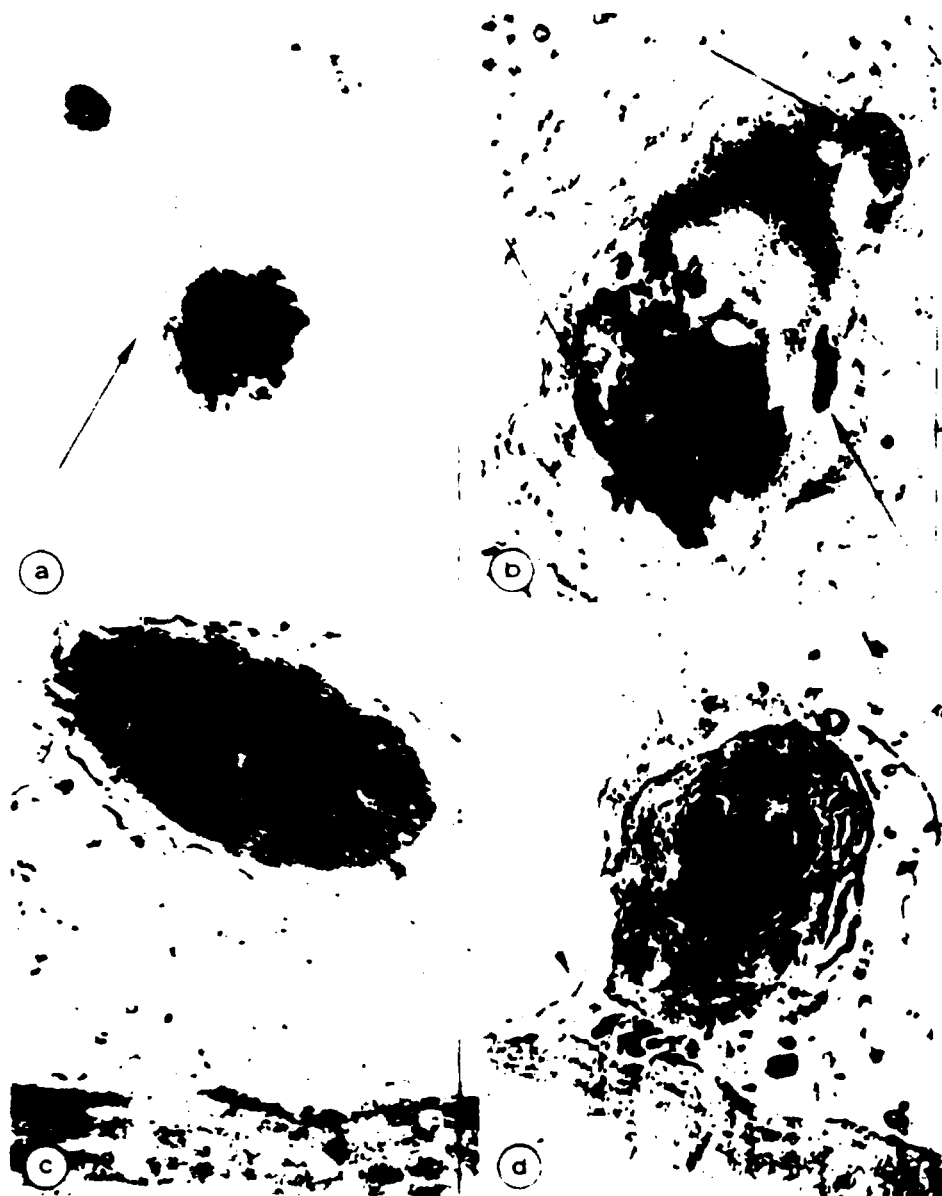


Fig. 1. Transmission electron micrographs of lead deposits in corn roots after 6 days of treatment (see ref. 31 for details). Line scales in all Figs. represent $1\text{ }\mu\text{m}$. (a) Small deposit surrounded by a membrane (arrow). (b) Dictyosome vesicles containing cell wall material fusing with a deposit (arrows). (c) Deposit nearing cell wall. (d) Membrane surrounding deposit fusing with plasmalemma (arrow).



Fig. 2. Transmission electron micrographs of lead deposits in corn plants. Line scales represent 1 μ m in all Figs. (a) Wall around deposit fusing with wall of root cell (arrow). (b) Typical appearance of deposits in root tip cell walls. Note unevenly thickened cell wall. (c) Typical appearance of deposits in older portions of root. (d) Deposits in corn leaf. Note relationship to cell wall. (For additional information see ref. 31).

mitochondria bound 58 nmoles of Cd per mg of mitochondrial protein. Cadmium uncoupled oxidative phosphorylation and inhibited substrate oxidation of isolated corn mitochondria^{9,36}. While work with artificial electron acceptors shows a clear inhibition of dehydrogenase activity³⁶, further studies with the artificial electron donating system of tetramethyl-P-phenylenediamine dihydrochloride - ascorbate indicate the likelihood of Cd-induced inhibition of electron transfer at the terminal oxidase (G. Eisinga and D. E. Koeppe, personal communication). In all studies, dithiothreitol prevented any effect of Cd, and the presence of phosphate greatly reduced it.

The reports of subcellular Pb effects in plants are very limited. Lead does bind to many membranes as already indicated (see also ref. 10). This binding has been quantitated in isolated corn mitochondria⁹ and is closely correlated with the inhibition of succinate oxidation²⁴, the stimulation of exogenous NADH oxidation⁹, and the increased swelling observed spectrophotometrically⁹. Electron transfer in the photosynthetic light reaction of isolated chloroplasts is also inhibited by Pb³⁸.

Cd AND Pb EFFECTS IN VIVO

The most pronounced, and most often measured, effect of Cd on plants is that of dry weight. Substantial reductions in dry weight of corn, soybeans, and wheat have been reported with increasing soil or solution concentrations of Cd^{15,34,45}. A 50% inhibition of soybean top dry weight has been affected by soil concentrations of approx. 3-10 $\mu\text{g Cd/g dry weight}$ ^{15,34}. Substantially higher soil tissue concentrations of Cd were required before 50% reductions of corn roots and shoots were observed⁴⁵. The dry weight of wheat was affected by tissue concentrations of Cd comparable to those found in corn⁴⁵.

In soybeans Cd toxicity symptoms resemble those of Fe chlorosis, while wheat plants showed no visual symptoms other than stunted growth¹⁵. Corn also exhibited a Cd-induced chlorosis that was correlated with a decrease in the concentration of leaf chlorophyll⁴⁵. This chlorosis was not due to a Cd-induced Fe deficiency as Fe concentrations were found to increase with increasing tissue concentrations of Cd⁴⁵. On the other hand, Zn concentrations decreased as tissue concentrations of Cd increased, which results in an increased Fe/Zn ratio. The metabolic functions of Fe are known to be associated with the supply of Zn⁴⁶; thus if Zn and Cd were competitive ions as suggested by work by Lagerwerff and Biersdorf³⁷, the uptake of Fe would be affected by an increase in the concentration of Cd.

The in vitro effects of Cd on the electron transfer reactions associated with chloroplasts and mitochondria are also observed in vivo. The net rate of photosynthesis was rapidly reduced when excised leaves of corn and sunflower were immersed in Cd-containing solutions^{7,8}. Reductions in stomatal opening and transpiration closely paralleled the reduction in net photosynthesis in sunflower⁷. Treatment of excised soybean root tips in 0.1 mM CdCl₂ reduced the

impede the movement and effect of Cd and Pb. This impediment by environmental and physiological factors is, however, much greater for Pb than Cd. The potential danger, then, of toxicity and its ramifications, does indeed seem to be greater for Cd than Pb, even though environmental concentrations of Pb are today considerably higher.

ACKNOWLEDGMENTS

The author gratefully acknowledges the helpful assistance of many people in preparing this paper, especially that of Dr. Raymond J. Miller and Dr. C. P. Malone. Some of the research was supported by a NSF-RANN grant to the University of Illinois and by the Illinois Agricultural Experiment Station.

REFERENCES

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LEAD AND CADMIUM LEVELS IN SOIL AND PLANTS NEAR HIGHWAYS AND THEIR CORRELATION WITH TRAFFIC DENSITY

M. RODRIGUEZ-FLORES & E. RODRIGUEZ-CASTELLON*

Department of Chemistry, University of Puerto Rico,
Mayaguez, Puerto Rico 00708

ABSTRACT

Lead and cadmium pollution in zones adjacent to some roads in Puerto Rico has been studied. The levels of these metals in soil and vegetation are much higher than typical background concentrations. Integration of the concentration vs. distance curves along transects perpendicular to the roads yields areas proportional to the heavy metal burden of the roadside soil and vegetation. These areas exhibit a significant correlation with the vehicular traffic density and it is shown that they represent more accurately the severity of pollution than the maximum levels at the same locality. It was found that wind direction affects the distribution of Pb along a transect. Also, the Pb and Cd concentrations in soil and the Pb concentration in vegetation fall off rapidly with increasing distance from the roads, in agreement with previous investigations. Accumulation of Pb and Cd above background levels seems to take place up to a distance of approximately 33 m, giving rise to the suggestion that edible crops for human or animal consumption should be restricted within strips of this width on both sides of heavily travelled roads.

INTRODUCTION

Lead pollution arising from automobile exhaust fumes has been amply studied during the last two decades, but cadmium pollution due to abrasion of automobile tyres and some oils (Lagerwerff & Specht, 1970) has not received the same scrutiny

Puerto Rico has an area of 8960 km². The number of registered motor vehicles exceeds one million units, indicating one of the highest motor vehicle concentrations

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areas have high traffic densities, and vegetation.

Gasoline is one of the cheapest sources of Pb. The Pb content of gasoline is 0.19 g litre⁻¹ (Smith, 1976). Data concerning Pb emission from gasoline are 81 mg km⁻¹ (Smith, 1976); a conservative estimate of 25 mg km⁻¹ (Ter Braak, 1976) is the best approximation to the actual value. The mean yield is 6.34 km litre⁻¹.

Pb emission. The Pb content of gasoline has increased considerably if the increase in

the vehicular traffic density as measured by Shuck & Locke (1970). Ganje and others (1970) found that the Pb levels in soil and vegetation are affected by the distance from the road, the season of the year, and the effect of Pb discharge from the road's edge — measured from the road's edge — along a width of 100 m. Lead levels in soil, whose Cd content varies (Shuck & Locke, 1970). The dynamics of Cd

transport to soil and vegetation differ from those of Pb; the former reaches the soil mainly in runoff water and not through an aerial route. Ward *et al.* (1977) have found a significant correlation between traffic density and Cd levels in the soil and vegetation of the median strips of roads.

In order to investigate the influence of traffic density upon Pb and Cd levels in the roadside soil and vegetation, several sites were selected with traffic densities varying from 630 to 72,250 vehicles day⁻¹.

Most of the sampling was done on the western part of the island of Puerto Rico, but a site along public road 3, between Rio Piedras and Carolina, was included in the study because it is one of the most heavily travelled roads in Puerto Rico. Relevant data about the sampled zones are included in Table 1. The soils are predominantly Coloso silty clay loam, Lares clay, and Rio Piedras clay. The most abundant plant species are *Chenchrus echinatus* L., *Sorghum halopense*, *Paspalum paniculatum* L., and *Stipa ichu*.

METHODS AND EXPERIMENTAL PROCEDURES

Soil and plant samples were taken on both sides of the road at distances of 3, 10, 20 and 33 m, in a line perpendicular to the road. A 'background' sample was taken beyond 100 m and, occasionally, an additional sample was taken at 66 m. Soil samples were taken at the surface, at a maximum depth of 5 cm. Plant samples included only the aerial parts.

All samples were put in plastic bags and stored at a temperature of 4 °C until analysed. The soil samples were allowed to dry at room temperature. Once dried, they were ground in a porcelain mortar and passed through a 2-mm sieve. Twenty-five-gram samples of soil were then treated with 50 ml of 1N HCl, allowed to stand for 24 h at room temperature, and then stirred in a mixer for 1 h and filtered. The filtrate was stored in a plastic bottle, ready for analysis.

Plant samples were dried in an oven at 95 °C for 2 days, then ground and put back into the oven for further drying. Two-gram samples of dry plant material were weighed into 150-ml beakers, followed by addition of 50 ml modified aqua regia (three parts concentrated HNO₃ to one part concentrated HCl). The beakers with the samples were covered with a watch-glass and placed on a hot-plate. The digestion, performed at a temperature of 90–95 °C, was continued until a volume of 1 ml was reached. Then, 25 ml of 30% H₂O₂ were added. This mix was allowed to evaporate down to a volume of 3 ml, after which 5 ml of 2N HCl were added.

Further heating was used to reduce the volume to 3 ml. After cooling, the solution was filtered to remove small quantities of waxy (cerous) solids and distilled water was added to attain a final volume of 10 ml. The Pb and Cd contents of the soil and plant extracts were determined by atomic absorption spectrophotometry using a Perkin-Elmer 303 model. Measurements were made at 228.8 nm for Cd and 283.3 nm for Pb.

SAMPLING SITES

W		E		N		S	
54	52	69	43	56	58	50	44
25	—	36	23	SiC	C	SiC	SC
2	159	9	9	February	November	1979	1979
40000	40000	72250	72250				

US (NBS) ORCHARD

$Cd (\mu g g^{-1})$
0.11 ± 0.02
0.12 ± 0.05

employed for plant material, a
of Standards orchard leaves
ving the results of replicate
r vegetable matter, although a
Pb. This could be explained in
and the digestion procedure not
ution.

le for Cd and Pb analysis the
ly on the basis of 12 replicate
osen for this procedure gave a
 $0.1 \mu g g^{-1}$ for Cd and precisions

IN

their Cd and Pb content as
ted in Table 3—all entries are
mple.

creases in an exponential-like
distances where samples were
s metal. The Pb concentration
33 m, where nearly constant
off with distance is much more
most all of the total Pb burden
of 33 m

it with distance, however, the
exhibit a definite trend. An
side of Zone III, in which the
n this zone had pH values that
at 33 m). The anomalous Cd
bility (and availability) of Cd at
iter distances. This observation
ho studied the influence of pH

TABLE 3
LEAD AND CADMIUM CONTENTS OF ROADSIDE SOIL AND PLANTS AS A FUNCTION OF DISTANCE FROM THE ROAD

	Distance (m)	Site									
		I W	II W	II E	III W	III E	IV W	IV E	V W	V E	
Ph (soil) ($\mu g g^{-1}$)	3	21.0	679.0	522.0	906.0	511.0	913.0	676.0	989.0	790.0	
	10	19.4	17.9	10.1	111.0	—	102.0	168.0	78.6	297.0	
	20	9.8	30.8	9.4	29.7	12.0	29.0	99.9	308.0	52.5	
	33	11.0	23.0	5.5	17.6	12.1	34.1	58.5	282.0	65.9	
	66	—	—	—	13.4	7.2	18.3	11.4	—	—	
	Bk*	10.8	—	—	13.6	6.0	12.0	11.7	12.4	12.5	
Pb (plant) ($\mu g g^{-1}$)	3	13.7	99.0	13.4	40.0	22.4	68.7	128.0	311.0	208.0	
	10	7.0	13.6	7.6	19.3	—	32.7	29.5	51.3	31.4	
	20	3.0	12.6	5.0	16.4	9.4	19.3	17.7	52.9	17.4	
	33	3.0	7.5	3.6	5.8	6.9	16.5	12.1	15.7	11.6	
	66	—	—	—	8.3	2.9	10.0	7.7	—	—	
	Bk	3.0	—	—	5.9	2.9	5.9	5.9	10.1	9.0	
Cd (soil) ($\mu g g^{-1}$)	3	0.09	0.93	0.86	0.84	0.76	0.85	0.60	0.76	0.61	
	10	0.09	0.20	0.20	0.40	—	0.30	0.24	0.40	0.40	
	20	0.06	0.16	0.17	0.29	0.31	0.36	0.33	0.47	0.20	
	33	0.07	0.18	0.28	0.29	0.30	0.34	0.31	0.45	0.12	
	66	—	—	—	0.24	0.24	0.28	0.23	—	—	
	Bk	0.07	—	—	0.28	0.22	0.28	0.17	0.39	0.13	
Cd plant ($\mu g g^{-1}$)	3	0.31	2.47	0.90	0.30	0.35	0.81	0.90	0.73	0.57	
	10	0.21	0.37	0.40	0.24	—	0.45	0.44	0.42	0.50	
	20	0.20	0.40	0.57	0.39	0.50	0.35	0.73	0.40	0.32	
	33	0.16	0.25	0.52	0.47	1.67	0.59	0.61	0.25	0.25	
	66	—	—	—	0.23	0.29	0.57	0.32	—	—	
	Bk	0.18	—	—	0.20	0.17	0.21	0.13	0.23	0.12	

* Bk, background.
* Air-dry weight basis.
* Oven-dry weight basis.

The Pb contents of soil and vegetation are, in some cases, very high, particularly near the roads with the heaviest traffic. In Table 3 a big difference can be seen between the levels in Zone I, with 630 vehicles day⁻¹ and those of Zones IV and V, having much greater traffic densities. The Pb levels for vegetation in Zones IV and V are considered to be very high and represent a serious threat to domestic animals that feed partially or totally on this vegetation. Hammond & Aronson (1964) indicated that a daily diet containing from 6 to 7 mg of Pb per kg of body weight was toxic, and possibly fatal, to cattle. In most of the zones investigated the Pb levels closest to the roads are such that this value could be attained under ordinary circumstances.

The Cd levels in soil and vegetation are high and very similar to those found in the US by Lagerwerff & Specht (1970).

The distributions of both Cd and Pb are suggestive of automobile traffic as the source of pollution. In order to test this hypothesis for the case of Pb, the assumption was made that the total Pb burden of the soil and vegetation at a given location should be proportional to the integral of the concentration vs. distance

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LEAD AND CADMIUM IN SOIL NEAR HIGHWAYS

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RELATIONSHIP VS. TRAFFIC DENSITY

	IV		V	
	E	W	E	S
4	0.96	1.65	3.56	1.69
11	0.17	0.34	0.86	0.50
18	0.28	0.24	0.40	0.29
41	0.63	0.72	0.51	0.40
	2.61		5.25	
	0.51		1.36	
	0.52		0.69	
	1.35		0.91	
	40000		72250	

determine the area, a graphical method was used. The lower and upper limits, the smallest distance of measurement, were determined at which the background levels from the upwind and downwind, the sum of the corresponding lead burden at a particular site, for relative to some convenient value) of traffic densities and the coefficients were calculated, the first and the second using the log-log method. The direct data gave $r = 0.9941$ at which was improved by using the log

better correlation: $r = 0.9781$ at $p < 0.001$ and $r = 0.9637$ at $p < 0.0025$.

along transects perpendicular to the sampled sites for Cd and Pb. The correlation with the average daily traffic

together with the regression support for the original hypothesis and ($r = 0.552$, $p < 0.10$) was not of several effects—the lower Cd level to measure accurately the background levels and, since Cd is

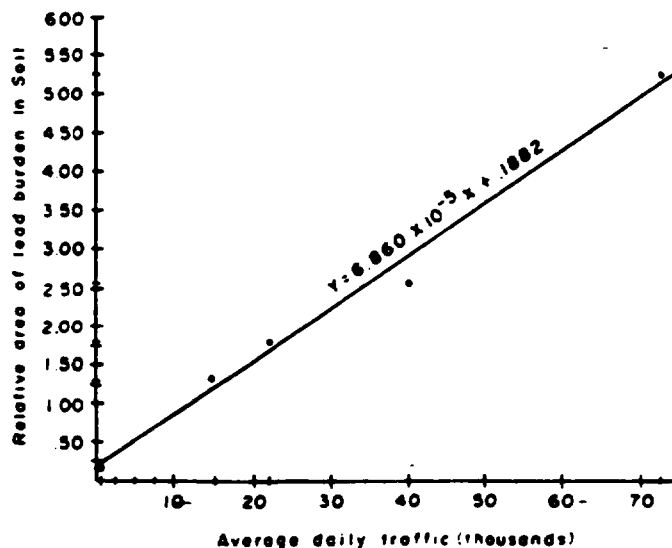


Fig. 1 Observed correlation between traffic density and relative area of lead burden in soil $r = 0.9941$ ($p < 0.001$)

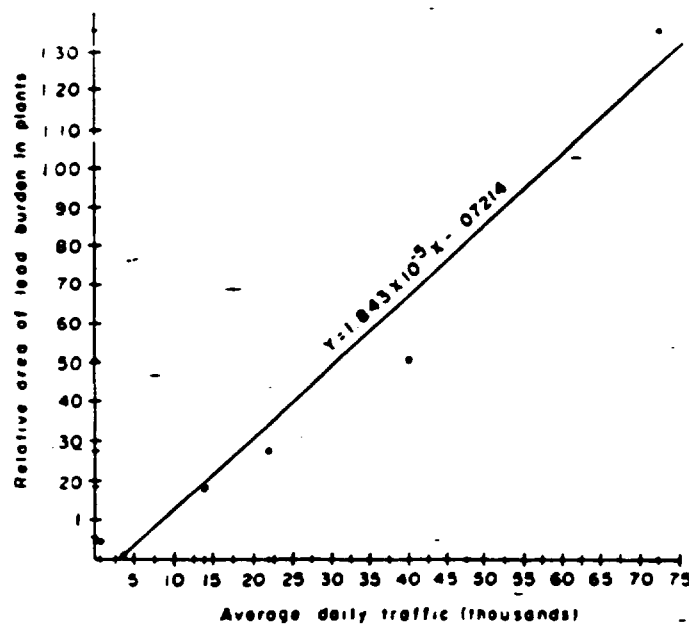


Fig. 2 Observed correlation between traffic density and relative area of lead burden in plants $r = 0.9781$ ($p < 0.001$)

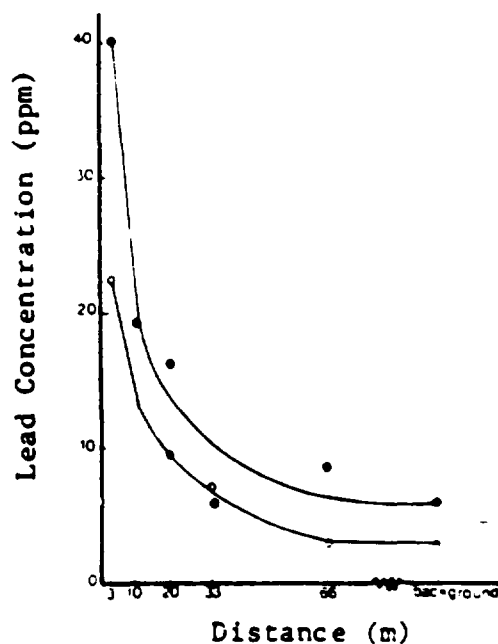


Fig. 4 Effect of wind direction on lead levels in plants alongside highway no. 2, 147 km, with 22 100 vehicles day⁻¹ ●, downwind side; ○, upwind side

predominant wind component blows from the east during all seasons. It is readily seen that the Pb discharge areas of soil and vegetation are larger for the western sides of both zones (Figs 3 and 4, and Table 4); this constitutes evidence supporting an aerial route for the dispersion of Pb throughout the ecosystems near the roads. At the same time, it is evident that the Cd distribution is independent of wind direction, the reason being that this metal is mainly transported via runoff waters.

The Pb/Cd concentration ratios for soil, averaged through all distances from the road, exceed the corresponding ratios for vegetation by factors of 7.2, 8.2, 14.8, 4.9, 7.1, 6.0, 7.6, 2.9 and 3.1 in Zones I, I, II-W, II-E, III-W, III-E, IV-W, IV-E, V-N and V-S, respectively. This is an indication of the preferential uptake of Cd by plants. These results confirm the findings of Lagerwerff & Specht (1970), who have dealt with their toxicological implications.

CONCLUSIONS

The Cd and Pb levels in soil and the Pb levels in vegetation decrease with increasing distance from the roadside. However, the Cd levels in vegetation do not exhibit a regular gradient as the distance from the road increases.



(m)
side highway no. 2, 147 km, with 22 100
wind side

tribution in the environment
of Pb

ific and the areas under the
suggests that the latter quantities
pollution than the maximum levels
from the road. Zone IV (40 000
 $\mu\text{g g}^{-1}$ on the upwind side and
corresponding values for Zone V
and 390 $\mu\text{g g}^{-1}$. At first sight, Zone
n to be more heavily polluted.
are considered, the ratio of their
ording to this criterion, the zone
with Pb

on the distribution of Pb in the
if their flat terrain, the absence of
their proximity to airports, where
it the year. For these zones, the

In Parr, J. F. et al. (eds.). 1982. Land Treatment of Hazardous Wastes. Noyes Publ., Park Ridge, N.J. 426 pp. (In Press).

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POTENTIAL EFFECTS OF WASTE CONSTITUENTS ON THE FOOD-CHAIN

R. L. Chaney

Persistent negative impacts on humans, agriculture, or environment from water-borne toxic chemicals would be the basis for prohibiting treatment of a waste, or a management or closure technique for a land treatment site. This chapter considers food-chain pathways for effects of hazardous waste land treatment, based on long experience with natural toxicants and recent experience with land application of sewage sludge and other wastes. We must separate our interpretation of this information for clearly distinct aspects of land treatment: 1) during site operation; 2) during the closure period; and 3) persistent beyond closure. It seems clear that many wastes can be managed at land treatment sites if the wastes are sufficiently characterized, and site personnel appropriately trained.

Macronutrients

Potential Beneficial Animal Responses--

Many sludges formed during treatment of industrial wastewater will contain sufficient amounts of macronutrients (N, P, K, Ca, and Mg) to act as fertilizers. Plant yields reach maximum levels when macronutrients are provided at optimum levels; hence, when wastes are used to supply the required nutrients, the wastes are fertilizers. A recent USDA report (USDA, 1978) discussed N, P, and K supply from wastes.

Besides increase in crop yields, crops grown with adequate supply of a nutrient have higher levels of that nutrient in their shoots than do plants whose yield is limited by inadequate supply of that nutrient (Bates, 1971).

Crop species and cultivars differ in response to nutrient supply and in forage nutrient levels (Hill and Guss, 1976; Reid and Horvath, 1980). Animal response (weight gains and health) to ingesting a crop is greater when that crop supplies needed macronutrients (Reid and Jung, 1974); further, forage protein content is dependent on N supply. Thus, land application of wastes to supply the macronutrient fertilizer requirements of forage crops can benefit livestock.

Potential Toxicity and Mineral Imbalances--

In contrast to the situation described above in which good management practices allow use of wastes at rates to supply crop macronutrient requirements, poor waste, soil, crop or animal management can lead to several problems. The problems fit a general group: excess supply of one nutrient causes imbalance in soil, crop, and/or animals leading to lower rate of weight gain and even specific animal health problems. The recent review by Reid and Horvath (1980) discusses these phenomena fairly comprehensively.

Grass tetany--Cattle and sheep with magnesium deficiency (hypomagnesemia) suffer a potentially lethal disease called grass tetany. This is a complex animal response in which soil, fertilizers, environment, and plant and animal characteristics all influence severity. Several valuable reviews discuss these many factors (Grunes, Stout, and Brownell, 1970; Grunes, 1973; Reid and Jung, 1974; Rendig and Grunes, 1979; Wilkinson et al., 1972; Reid and Horvath, 1980). Forages with Mg less than 0.20%, and with the ratio $K:(Ca+Mg)$ (on an equivalent basis) greater than 2.2, with K greater than 2.5%, and high N generally cause grass tetany in susceptible animals.

The disease occurs on selected soil types (Kubota, Oberly, and Naphan, 1980). Many forage grasses can reach a nutrient composition which will cause the disease; further, cultivars of a crop also differ in tetanigenic potential (Thill and George, 1975; Grunes, Stout, and Brownell, 1970; Sleper et al., 1980; Brown and Sleper, 1980; Mayland, Grunes, and Lazar, 1976; Karlen et al., 1978). Fertilization with N to increase forage yield sometimes increases tetanigenic potential by increasing K uptake (Follett et al., 1975).

Environmental conditions play a dominant role in grass tetany. Nearly all cases result from forage grasses grown on seasonally wet or poorly drained, cool soils. Several plant and soil factors are altered under these conditions. First, wet soils have a higher $K:(Ca+Mg)$ ratio in their soil solution due to Donnan equilibrium control of cation exchange reactions; thus wet soils provide more K and less Mg than do dry soils (Karlen et al., 1978, 1980a, 1980b). Second, wet

soils have low O_2 supply, which limits cation absorption by roots and also limits root exploration of the soil (further limited by cool temperatures). Wet, low O_2 soils provide more K and less Mg to forage grasses than do dry soils (Elkins et al., 1978). Cultivar differences in Mg level and K:(Ca+Mg) are much greater under low O_2 conditions, even when the soil has normal water content (Elkins et al., 1978; Haaland, Elkins, and Hoveland, 1978).

Both low O_2 and cool, wet soils act to increase K:(Ca+Mg) in forages and thus their tetanigenic potential. This happens even though soil Mg status is at recommended levels for crop production. Use of dolomitic (high Mg) limestone seldom counteracts grass tetany, although MgO application may help if K supply is not excessive. Adequacy of soil Mg is generally judged by a consideration of both exchangeable Mg and exchangeable Mg as a fraction of the total exchangeable cations (Doll and Lucas, 1973). Soil K status is similarly evaluated, with greater emphasis on exchangeable K as a fraction of the total exchangeable cations. Obviously, high soil K status is more likely to cause tetanigenic forage than is normal soil K status.

Repeated annual application of poultry manure (high in K and N) to fertilize tall fescue led to high incidence of grass tetany in cattle (Stuedemann et al., 1975). Soil K levels rose while soil Mg was decreased by crop removal (Jackson, Leonard, and Wilkinson, 1975).

Application of other wastes, lower in K, would not be expected to cause grass tetany easily; soil, environmental, and crop factors should be managed carefully to avoid tetany. If poorly drained soils are selected for a land treatment site, greater management is clearly needed.

Cattle often reject Mg supplements offered ad lib. to correct forage K:(Ca+Mg) imbalance. Stuedemann et al. (1974) reported a practical method to correct this problem; a slurry of MgO and bentonite is sprayed on the forage, with the bentonite added to improve adherence (see also Stuedemann et al., 1975). Cattle grazing treated pastures maintained normal Mg status while cattle on the control treatment experienced grass tetany.

Fat necrosis--A disease called fat necrosis reduces weight gain of cattle grazing high K status tall fescue (Williams, Tyler, and Papp, 1969). Fat necrosis occurred at much higher rate in cattle grazing poultry manure fertilized, than NH_4NO_3 fertilized, tall fescue (Stuedemann et al., 1973, 1975). The crop species which have caused fat necrosis are very limited (mostly tall fescue); further, it does not

need cool, wet soils which are needed for expression of grass tetany. Land treatment sites using tall fescue as cattle feed will need to manage soil K status reasonably.

Others--Domestic livestock often suffer Ca:P imbalance problems if they do not receive concentrated supplements when ingesting Ca:P imbalanced forages (Reid and Jung, 1974; Reid and Horvath, 1980; Baker and Chesnin, 1976). Bone development and arthritis problems result if Ca:P imbalance is not corrected. Research has been conducted to select crop cultivars which prevent imbalance (Hill and Jung, 1975).

Wastes very high in $\text{Fe}(\text{OH})_3$ (e.g., pickle liquor neutralization sludge) greatly increase P adsorption capacity in acidic soils. This in turn would reduce forage P concentration, and even reduce crop yield (Nelson, D. W. 1980. Lafayette, Ind., personal communication). Some industrial biological sludges are low in P, and supplemental P fertilizer would be required to achieve optimum crop yield and P concentration. On the other hand, P concentration in sludge fertilized crops is not increased to excessive levels which would cause crop or animal P toxicity even when sewage sludge supplies quite high available P in soils.

Pathways for Transfer of Toxic Chemicals in Wastes to the Food-chain

Liquid sludges can be spray-applied to cropland and tilled into the soil. Alternatively, liquid sludge can be sprayed onto forage or pasture land where it can contact plants and/or remain on the soil surface. Dewatered or dried sludges or composted wastes can be applied and mixed with or remain on the soil surface. These management options allow substantially different quantities of waste-borne toxic chemicals to enter the food chain, by quite different routes. Some options allow animals to directly ingest sludges, while other options use reactions in soils and properties of plants to largely prevent exposure.

Sludge Adherence to Existing Crops--

When liquid sludges (0-10% solids) are sprayed on pastures or forage crops, a thin film of the sludge coats the plant foliage. Research has found that some wastes dry and adhere strongly while others dry and flake off upon weathering. The first records of organic waste adherence came from a study of land application of high copper pig manure slurry (Batey, Berryman, and Line, 1972); forage grasses were enriched in Cu due to adhering manure.

Based on these findings, research was begun on sewage sludge adherence to forage crops and effects on grazing

cattle. Chaney and Lloyd (1979) found that once liquid digested sludge dried on tall fescue forage it was not readily washed off by rainfall. Growth of the crop biomass diluted the sludge percentage in harvested forage. Sludge adherence was greater at higher application rates. Jones et al. (1979) found that sludge could be washed off forages before it dried, but not after. They also found that the amount of adhering sludge was approximately a linear function of the %-solids of the applied liquid sludge.

Sludge has adhered to all crops studied (Chaney and Lloyd, 1979; Lloyd and Chaney, unpublished; Jones et al., 1979; Bertrand et al, 1981). Sludge adherence is easily characterized since the levels of some microelements in sludge-contaminated forage are much greater than levels ordinarily possible by uptake-translocation by forage plants. Plant uptake and translocation to shoots of Cu, Pb, Cr, Fe, etc., is so limited that high levels of these elements indicates direct sludge contamination (see Chaney and Lloyd, 1979). Many early reports on uptake of microelements from surface applied sludges presumed uptake when in fact sludge adherence fully explains their observations (Boswell, 1975; Fitzgerald, 1978). Industrial aerobic sludges adhere to forages in a manner similar to that of sewage sludge (Chaney and Hornick, unpublished results).

Another route for entry of microelements into the food chain is through farm equipment. Studies with pig manure indicate that organic wastes on the soil surface can be lifted and mixed into baled hay (Dalgarno and Mills, 1975).

When increased levels of microelements in forage indicate sludge adherence, all constituents present in the sludge contaminate the forage. Not only microelements, but also macroelements, pathogens (Brown, Jones, and Donnelly, 1980), and toxic organics (Fitzgerald, 1978) are increased.

Ingestion of Sludge-amended Soil or Sludge on the Soil Surface--

Several research programs have established that grazing animals consume soil as a part of the normal grazing process. Teeth of sheep and cattle wear out more rapidly when the forage is contaminated with soil (Healy and Ludwig, 1965; Nolan and Black, 1970). Study of the teeth wear problem led Healy (1968) to more fully develop Field and Purves' (1964) method of soil ingestion measurement in which the Ti level in forage and feces is compared to that of soil. Titanium present in soil is not appreciably absorbed and translocated by plants. Forage Ti level thus becomes a label for soil in/on forages. Healy, Rankin, and Watts (1974) found that wet weather and excessive stocking rates

caused forages to be trampled into the soil, thereby increasing soil adherence to forages. Although soil was normally 1-2% of sheep's diet, it reached 24% in the worst cases. In other research, Mayland et al. (1975) and Mayland, Shewmaker, and Bull (1977) found that cattle grazing on dryland-grown crested wheatgrass consumed considerable quantities of soil. Because the cattle consumed plants complete with soil-laden roots, the ingested diet contained 20% soil. Silage contains soil as well, and the soil can interfere with microelement availability (Lamand, 1979). Fries et al. (1982) have recently reviewed soil ingestion by dairy cattle.

Ingested soil can cause Pb poisoning of livestock when cattle graze soil naturally high in Pb (Egan and O'Cuill, 1970; Harbourn, McCrea, and Watkinson, 1968; Thornton and Kinniburgh, 1978). Even after closure of a smelter, Pb enriched crop residues remain on the soil surface, exposing cattle to possible Pb poisoning. Reclamation of Pb-smelter-polluted rangeland required incorporation of the organic sward thatch into the soil to prevent ingestion by cattle (Edwards and Clay, 1977).

Similarly, sewage sludge or composted sludge are ingested from the soil surface. Decker et al. (1980) found 6.5% (1977) and 2.0% (1978) compost in feces of cattle grazing sludge compost fertilized pastures. Compost did not adhere to the plant surfaces but lay on the soil surface.

Soil ingestion can also expose humans to waste-applied microelements in land treatment sites subsequently developed for housing. Some children and adults deliberately consume soil in a practice called "pica". If the soil is high in Pb (over 500-1000 ppm), individuals may absorb excessive amounts of Pb (Wedeen et al., 1978; Shellshear et al., 1975). Children also ingest soil and dust due to hand-to-mouth play activities and by mouthing of toys, etc. This phenomenon is discussed in detail in the section on lead later in this chapter.

Soil or sludge ingestion can be an important process which allows entry of a sludge-borne microelement into the food chain especially when the element is normally not absorbed by plants (plant level soil level). For some elements (Zn, Cd, Mn, Se, etc.), plant levels often exceed soil levels, and plant uptake is a more important process than soil ingestion. However, soil ingestion is a potential route for allowing excessive Pb, Fe, Cu, F, As, Hg, Cu, Co, Mo, Se, and other elements into the food chain. Further, soil ingestion can interfere with availability of microelements in plants to animals. Individual elements will be discussed below.

Soil ingestion is an especially important pathway for persistent lipophilic toxic organic compounds. Harrison, Mol, and Healy (1970) found increased DDT in sheep grazing pastures where DDT was on the soil surface. They also studied lindane (Harrison, Mol, and Rudman, 1969; Collett and Harrison, 1968). Bergh and Peoples (1977) noted PCB movement from surface applied dewatered sludge to milk of a grazing cow, but did not estimate sludge ingestion. Hansen et al. (1981) noted PCB retention by swine grazing a field where the surface soil was largely sewage sludge.

"Soil-Plant Barrier" to Microelements in the Food-Chain--

As discussed in the text regarding plant uptake of microelements, some elements are easily absorbed and translocated to food-chain plant tissues (e.g. Zn, Cd, Mn, Mo, Se, B), while others are not. These other elements are strongly bound to soil or retained in plant roots, and are not translocated to plant foliage in injurious amounts, even when soils are greatly enriched (e.g. Fe, Pb, Hg, Al, Ti, Cr^{3+} , Ag, Au, Sn, Si, Zr). Even though an element may be easily or relatively easily absorbed and translocated to plant foliage, phytotoxicity may limit plant levels of these elements to levels safe for animals (e.g. Zn, Cu, Ni, Mn, As, B).

During the last 40 years, these concepts were developed by many researchers. Important reviews of the research supporting these concepts have been prepared but had not named the general theory (Underwood, 1977; Allaway, 1968, 1977a, 1977b; Bowen, 1966, 1979; Baker and Chesnin, 1976; Chaney, 1980; Lisk, 1972; Kienholz, 1980; Loneragen, 1975; Reid and Horvath, 1980; Cataldo and Wildung, 1978; Leeper, 1978; Ammerman et al., 1977; Shacklette et al., 1978; Beckett and Davis, 1979; Page, 1974; and Walsh, Sumner, and Corey, 1976). Chaney (1980) introduced the term "Soil-Plant Barrier" to describe these concepts when considering waste-soil-plant-animal relationships of toxic microelements. A "Soil-Plant Barrier" protects the food chain from toxicity of a microelement when one or more of these processes limit maximum levels of that element in edible plant tissues to levels safe for animals: 1) insolubility of the element in soil prevents uptake, 2) immobility of an element in fibrous roots prevents translocation to edible plant tissues, or 3) phytotoxicity of the element occurs at concentrations of the element in edible plant tissues below that injurious to animals.

Unfortunately, the "Soil-Plant Barrier" does not protect animals from toxicities of all elements. The exceptions important in assessing risk from land application of municipal sludge are Cd, Se, and Mo; a few more elements may

have to be considered for land application of industrial wastes (Be, Co). Ingestion of amended soil or sludge can circumvent the "Soil-Plant Barrier". Many elements are so insoluble or non-toxic that animal health is not influenced even if ingested soil or waste contains the element (e.g., Cr^{3+} , Zr, Ti, Al, Sn, Si). However, direct ingestion of soil or wastes rich in some elements (e.g., Cu, F, Zn, Pb, Fe^{2+} , As, Co, and Hg) allows risk to livestock when risk would have been insignificant if the sludge were mixed with the surface soil (0-15cm). These concepts will be applied in considering risk to the food chain from individual microelements applied in wastes (see below).

Interactions Among Dietary and Sludge Constituents Influence Microelement Impact on Food-Chain--

Evaluation of the potential impact of microelements on animals via their consumption of sludge, sludge-amended soil, or crops grown on sludge-amended soil, is very complex. Animal species differ in tolerance of microelements. Tolerance to microelements is also influenced by age; younger animals are generally more sensitive than older. Crop species absorb unequal amounts of microelements. Total and relative microelement uptake is affected by crop species and cultivar, soil pH, organic matter, soil temperature and other factors. Wastes differ in levels of elements and ratios among elements. Individual potentially toxic elements interact with other elements in the diet, often reciprocally. These interactions are often the basis for physiological toxicity; hence, interactions are of great importance in assessing risk.

Interactions affecting Cu deficiency in ruminant animals were among the first studied, and have been intensely examined because of their practical significance. Animals can experience simple Cu deficiency, Mo-induced, sulfate-induced, or Zn-, Cd-, or Fe-induced Cu deficiency. Among the most complex is the 3-way Cu-Mo-S interaction. Dietary sulfate is reduced to sulfide in the rumen; sulfide reacts with Mo to form a thiomolybdate. Thiomolybdate reacts with Cu to form an insoluble compound which is unavailable and is excreted; this leads to depletion of liver Cu reserves and subsequently to clinical Cu deficiency (Mills et al., 1978; Bremner, 1979; Spence et al., 1980). Copper is of lower bioavailability in young forage plants than mature plants, and in fresh forages than in dried hay (Hartmans and Bosman, 1970). Forage species differ in bioavailability of Cu (Stoszek, et al., 1979). Soil consumed with forages reduces Cu absorption by sheep, perhaps due to soil Mo, Zn, or Fe but probably due to Cu sorption by soil constituents preventing Cu absorption in the intestine (Suttle, Alloway, and Thornton, 1975).

After the Cu-Mo-S interaction in ruminants was identified, it became clear that Zn, Cd, and Fe also interact with Cu bioavailability to both ruminants and monogastric animals (Bunn and Matrone, 1966; Hill et al., 1963; Matrone, 1974; McGhee, Creger, and Couch, 1965; Mills, 1974, 1978; Standish et al., 1971; Standish and Ammerman, 1971; Suttle and Mills, 1966). Reciprocally, high dietary Cu interacts to reduce absorption and toxicity of Zn, Fe, and Cd (Bunn and Matrone, 1966; Grant-Frost and Underwood, 1958; Cox and Harris, 1960; Lee and Matrone, 1969; ~~L'Estrange, 1979; McGhee, Creger, and Couch, 1965~~). Other elemental interactions have been studied and found to be important in assessing risks (Underwood, 1977; Matrone, 1974; Levander, 1979; NRC, 1980b; Mills and Dalgarno, 1972; Mills et al., 1980; Mahaffey and Vanderveen, 1979; Fox, 1974, 1979; Fox et al., 1979; Bremner, 1979.)

In many cases, food chain toxicity is a result of microelement imbalance as much as it is a result of increased supply of one potentially toxic element. When one element is so increased that the ratio of it to other elements or dietary constituents is great enough to induce a deficiency of another, then animal weight gain declines and a health effect is observed. Chaney (1980) noted that domestic sewage sludge contains a mixture of potentially toxic elements. Consumption of sludge or sludge-amended soil is a very different case for risk assessment than standard toxicological studies where a soluble salt of one element is added at rates to cause health effects (and often to purified rather than practical diets). With sludge ingestion, increased levels of dietary Zn are balanced by increased levels of Cu and Fe. Industrial wastes and sludge are a somewhat different case than domestic sewage sludge, because they are more likely to be enriched in only one or a few elements. The potential for microelement imbalances is greater with sludges rich in one element. Also, a wider range of elemental interactions must be considered to evaluate food chain impact of industrial wastes. A number of elements are considered below, in regard to sludge-soil-plant-animal interactions influencing the food chain.

Evaluation of Potential for Food-Chain Impacts of Individual Microelements Applied in Industrial Wastes--

A number of processes must be considered herein. Phytotoxicity and other aspects of the "Soil-Plant Barrier" must be considered in relation to maximum plant foliage levels of the microelement in question. Interactions should be considered through the complete sludge-soil-plant-animal system. Although not every element will be considered in detail, elements commonly present in sewage sludges and industrial wastes, and those EPA considered hazardous

constituents will be discussed.

An important reference for tolerance of microelements by animals has recently been published by the National Research Council (NRC, 1980b). The NRC committee considered increased levels of only the element being evaluated, although they discuss interactions. Their tolerance levels are shown in Table 8. Unfortunately, these levels may not be valid for sludge fertilized crops or for ingestion of sludge or soil because of the noted interactions.

Arsenic-- Arsenic is not essential for plants; however, since rats fed a highly purified diet show a response to low levels of As, the essentiality of As to animals is being intensely studied. Experience with As phytotoxicity comes mostly from pesticide residues in soil; sewage sludge is seldom a rich source of As. Substantial yield reduction due to As toxicity in most plants occurs under conditions which do not allow appreciable increase in As in edible crop tissues (Walsh and Keeney, 1975; Woolson, 1973). Rice and other crops grown on submerged soils are especially sensitive to As phytotoxicity (Deuel and Swoboda, 1972) because arsenate is reduced to the more toxic arsenite. Arsenic is somewhat increased in the peel of root crops at increased soil As, apparently due to soil contamination of the peel.

The food chain is protected from excess soil As applied in sludges because food and feed crops are not As-tolerant. Some rare plant species tolerate and accumulate As from As-rich soils (Rocovich and West, 1975; Porter and Peterson, 1975, 1977a, 1977b; Benson, Porter, and Peterson, 1981). Ingestion of As-rich industrial wastes from the soil surface could cause As toxicity to grazing animals and wildlife. This topic has not been studied although Porter and Peterson (1977b) noted animal deaths have occurred near As mine wastes.

In summary, phytotoxicity of soil As to crops prevents plant-borne As impacts on the food chain even in the garden soil scenario. Wastes rich in As are thus poor candidates for land treatment, due to phytotoxicity, and risks from direct ingestion.

Cadmium--Cadmium is not essential for plants. Although one study indicated Cd was essential for rats (Schwartz and Spallholz, 1978), it is not generally agreed that Cd is essential for animals (NRC, 1980b; Fox et al., 1979).

It now appears that Cd activity in most soils is controlled by adsorption rather than by formation of crystalline inorganic compounds (Street, Lindsay, and Sabey, 1977; Soon, 1981). Street, Lindsay, and Sabey (1977) found that $CdCO_3$

TABLE 8. MAXIMUM TOLERABLE LEVELS OF DIETARY MINERALS FOR DOMESTIC LIVESTOCK IN COMPARISON WITH LEVELS IN FORAGES

Element	"Soil-Plant Barrier"	Level in Plant Foliage ^{1/}		Maximum Levels chronically tolerate			
		Normal	Phytotoxic	Cattle	Sheep	Swine	Chicken
		---mg/kg dry foliage---		-----mg/kg dry diet-----			
As, inorganic	yes	0.01-1	3-10	50.	50.	50.	50.
B	yes	7-75	75	150.	(150.)	(150.)	(150.)
Cd ^{3/}	Fails	0.1-1	5-700	0.5	0.5	0.5	0.5
Cr ⁺³ , oxides	yes	0.1-1	20	(3000.)	(3000.)	(3000.)	3000.
Co	Fail?	0.01-0.3	25-100	10.	10.	10.	10.
Cu	yes	3-20	25-40	100.	25.	250.	300.
F	yes?	1-5	-	40.	60.	150.	200.
Fe	yes	30-300	-	1000.	500.	3000.	1000.
Mn	?	15-150	400-2000	1000.	1000.	400.	2000.
Mo	Fails	0.1-3.0	100	10.	10.	20.	100.
Ni	yes	0.1-5	50-100	50.	(50.)	(100.)	(300.)
Pb ^{3/}	yes	2-5	-	30.	30.	30.	30.
Se	Fails	0.1-2	100	(2.)	(2.)	2.	2.
V	yes?	0.1-1	10	50.	50.	(10.)	10.
Zn	yes	15-150	500-1500	500.	300.	1000.	1000.

1/ Based on literature summarized in text.

2/ Based on NRC (1980b). Continuous long-term feeding of minerals at the maximum tolerable levels may cause adverse effects. Levels in parentheses were derived by interspecific extrapolation by NRC.

3/ Maximum levels tolerated based on human food residue consideration.

can form in low cation exchange capacity, low organic matter, calcareous soils. Under anaerobic conditions, CdS forms in soil; CdS has very low solubility and is unavailable to plants (Takijima and Katsumi, 1973; Bingham et al., 1976b) but is readily oxidized in aerobic soil. Unfortunately, formation of CdS is not a practical management practice to minimize Cd uptake for crops other than rice.

A recent consensus review of Cd relationships in sewage sludge, soil, and plants summarized this complex topic (CAST, 1980). Of all soil properties affecting Cd level in plants, soil pH has the greatest effect. Increasing soil pH causes stronger adsorption of Cd by soil and reduces Cd uptake. Of other soil chemical properties, soil organic matter has been shown to have some effect; since higher organic matter reduces Cd uptake (e.g., White and Chaney, 1980). Other soil factors which affect Cd uptake include: temperature, soluble salts, chelators, and water status (Haghiri, 1974; Giordano, Mays, and Behel, 1979; Wallace et al., 1977; Bingham, 1980; Shaeffer et al., 1979).

The CAST (1980) report also summarized evidence which indicates that soil Cd remains crop available for a prolonged period after application. Availability to crops decreases only in calcareous soils. These conclusions are based on sludge field plots, sludge utilization farms, (CAST, 1980) and natural high Cd soils (Lund et al., 1981). Recent studies by Lloyd et al. (1981) indicated that sludge applied Cd remained nearly 100% labile many years after application.

Crops differ remarkably in their Cd accumulation, Cd tolerance, and translocation of Cd to edible plant parts (CAST, 1980; Bingham, 1979; Bingham et al., 1975, 1976a, 1976b; MacLean, 1976; Furr et al., 1976a, 1976b; Dowdy and Larson, 1975; Chaney and Hornick, 1978). Figure 7 shows Cd concentration in leaves and edible plant tissues of many crops grown on a neutral pH sludge amended soil containing 10 ppm Cd (based on data from Bingham et al., 1975, 1976a, 1976b). Tobacco, lettuce, spinach, chard, endive, cress, and turnip accumulate much higher foliar Cd levels than other leafy crops (e.g., kale, collards, cabbage). Although Cd in edible root of radish, turnip, and beet is only a small fraction of the Cd level in the shoots of the plants, carrot root Cd is about half of carrot leaf Cd. Similarly, the ratio (Cd in grain):(Cd in leaf) ranges from very low for corn to relatively high for wheat, oat, and soybean; Chaney, White and Tienhoven (1976) found that this ratio in soybean was reduced from >1 to <0.2 by increasing soil Zn.

The wide variation in crop tolerance of Cd causes difficulty in assessing the impact of soil Cd on the food

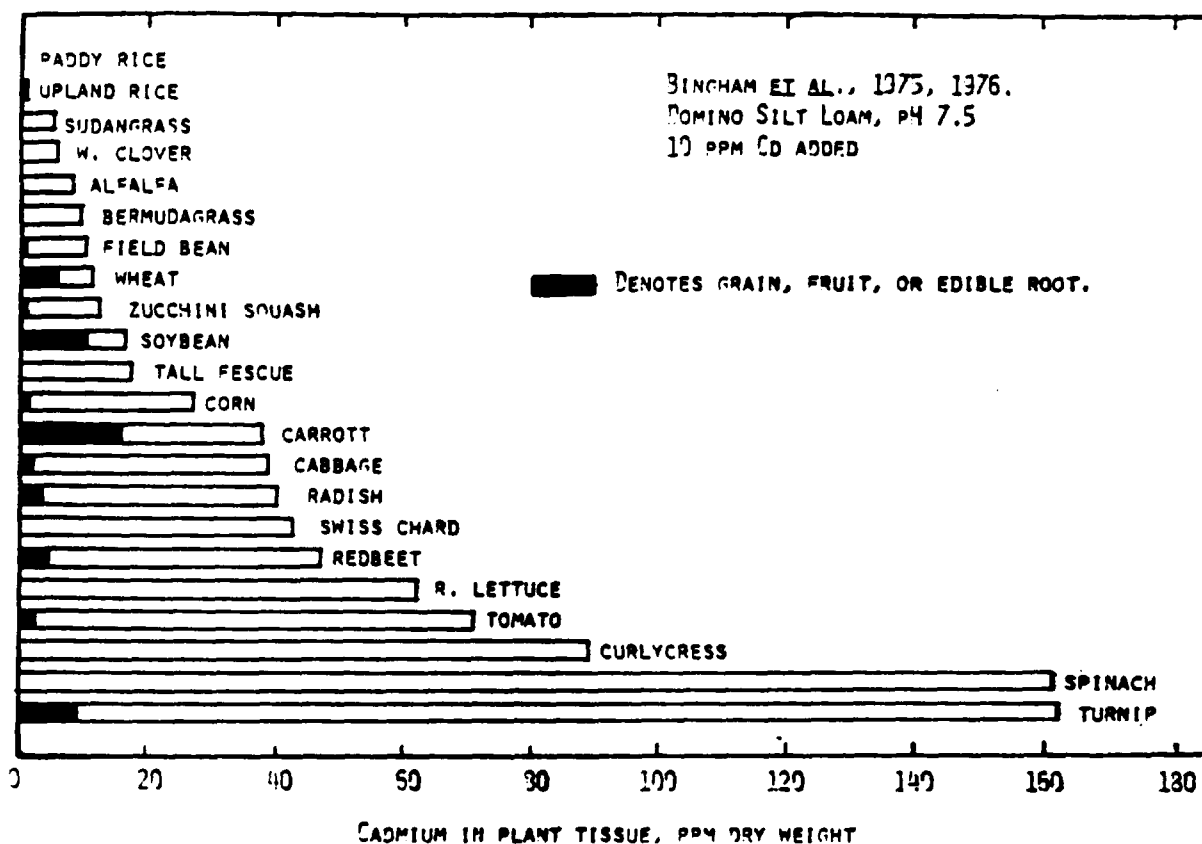


FIGURE 7. Crop differences in Cd accumulation. Crops were grown on calcareous Domino silt loam amended with 1% of a Cd-enriched sewage sludge (1000 ppm Cd) such that the amended soil contained 10 ppm Cd. Where a plant tissue other than leaves is normally eaten, its Cd concentration is shown by the black bar; foliar Cd for each plant is the full open bar (turnip leaves = 163 ppm Cd). (From Chaney and Hornick, 1978, based on Bingham et al., 1975, 1976a, 1976b).

chain. The foliar Cd associated with phytotoxicity (25% yield reduction) varies in different crops from 7 to 160 ppm dry weight (Bingham, 1979). Further, the foliar Cd concentration causing 50% yield reduction in lettuce and chard is greater in acidic soils (470 ppm in lettuce; 714 ppm in chard) than in calcareous soils (160 ppm in lettuce; 203 ppm in chard) (Mahler, Bingham, and Page, 1978). Some plants are unusually tolerant of Cd; Simon (1977) and Wigham, Martin, and Coughtrey (1980) have reported tolerance of Cd by ecotypes of grasses adapted to Cd-enriched Zn and Pb mining wastes. In summary, phytotoxicity of Cd does not limit crop Cd to acceptable levels.

Cadmium is an unusual and difficult case for evaluation of risk to the food chain. In contrast to other elements, Cd has a quite long biological half-life in humans -- generally considered 20 years. Absorbed Cd is bound to a low molecular weight protein to form metallothionein which is accumulated and retained in the kidney for a long period. High metallothionein-Cd in the kidney can lead to adverse health effects in the kidney.

Over one's lifetime, chronic food chain Cd exposure can cause different health problems than those experienced from acute exposure. Long-lived animals (e.g., humans) are at greater risk of this health effect than are short-lived animals (wildlife; domestic animals). Accumulation of Cd in organ meats (liver, kidney) was the basis for suggesting a low dietary Cd tolerance in domestic animals rather than a direct health effect to the animals (NRC, 1980b).

The potential risk of excess soil Cd to humans has been clearly documented. Adverse health effects resulted from prolonged consumption of foods grown locally on Cd enriched soils (Tsuchiya, 1978; Friberg et al., 1974; Fulkerson and Goeller, 1973; Hammons et al., 1978; Yamagata and Shigematsu, 1970; Kobayashi, 1978; Nogawa, 1978). A large number of Japanese farmers suffered Cd health effects after long-term ingestion of Cd-enriched rice grown in paddies polluted by Zn- and Pb-mining wastes or Zn-, Pb-, and Cu-smelter emissions in at least 7 different areas of Japan (Kobayashi, 1978; Takijima and Katsumi, 1973; Shigematsu et al., 1979; Kjellstrom, Shiroishi, and Evrin, 1977; Kojima et al., 1979; Saito et al., 1977; Nogawa, 1978; Nogawa, Ishizaki, and Kawano, 1978; Nogawa and Ishizaki, 1979; Nogawa et al., 1975; 1980). Rice Cd concentration and number of years exposure were both strongly related to the incidence rate of Cd health effects. A smelter enriched area in Belgium may have caused Cd-induced renal disease (Roel et al., 1981a) although route for exposure and increased kidney Cd have not yet been demonstrated.

The name "itai-itai" disease (translated as ouch-ouch disease) came from expressions of pain by elderly women suffering repeated bone fractures due to Cd-induced osteomalacia. Although the osteomalacia brought attention to this environmental Cd disease, severe osteomalacia does not frequently result in humans ingesting excessive Cd. Renal proximal tubular dysfunction (Franconi syndrome) is the first health effect of excessive chronic Cd exposure. The renal disease had high incidence in areas where Cd exposure was increased, and showed a dose-response relationship with Cd exposure (expressed as "Cd level in rice-times-years ingested"). All individuals with advanced itai-itai disease had severe proteinuria characteristic of the kidney disease. Renal disease subsequently proceeded to osteomalacia in some workers who ceased exposure when the kidney disease was identified (Kazantzis, 1979). However, this aspect of Cd disease is poorly understood. Sub-clinical osteomalacia is found in many of the Japanese farmers who experience renal disease (Mulawa, Nogawa, and Hagino, 1980).

Renal tubular dysfunction (Franconi syndrome) resulting from Cd ingestion is quite different from classic kidney failure. Franconi syndrome seldom proceeds to kidney failure requiring dialysis. Kjellstrom (1978) indicated that Franconi syndrome (low molecular weight proteinuria, glucosuria, aminoaciduria, phosphaturia, etc.) is the first Cd health effect; if Cd-exposure (rate-times-duration) is increased, kidney stones and osteomalacia/osteoporosis may result. Kjellstrom, Friberg, and Rahnster (1979) found greater mortality (shorter life span) in Cd exposed workers, but this may not be relevant to ingested Cd. Neither hypertension nor prostate cancer incidence are increased even when proteinuria is severe (Friberg et al., 1974; Doyle, 1977; Hammons et al., 1978; Tsuchiya, 1978; Ryan et al., 1979; Commission of the European Communities (CEC), 1978; Kjellstrom and Nordberg, 1978; Kjellstrom, Friberg, and Rahnster, 1979; Pahren et al., 1979; Lauwreys et al., 1980; Nogawa, 1978; Shigematsu et al., 1979). Although laboratory studies with rats and other animals have shown that anemia, enteropathy, and teratogenesis (due to Cd-induced Zn or Cu deficiency in the fetus) can result from ingested Cd, these are very unlikely with practical diets.

A number of researchers and groups have attempted to clarify the dose-effect and dose-response relationships for Cd (CEC, 1978; Friberg et al., 1974; Kjellstrom and Nordberg, 1978; Ryan et al., 1979; Tsuchiya, 1978; Hammons et al., 1976). The first sign of renal tubular dysfunction (increased excretion of B₂-microglobulin, a specific proteinuria characteristic of Cd injury) is generally agreed to occur at about 200 mg Cd/kg wet kidney cortex. Some

research indicates that the critical kidney cortex Cd level may be as high as 300 mg/kg (Roels et al., 1981b), but 200 mg/kg is the level generally accepted for use in risk analysis.

Kjellstrom and Nordberg (1978) developed a sophisticated multicompartmental dose-effect model for Cd metabolism in humans: "This present model predicted that a daily intake corresponding to 440 μg at age 50 would give 200 μg Cd/g of (wet) kidney cortex at age 45-50." These results were obtained by assuming a high, constant Cd concentration per unit calories, and that calorie (hence Cd) varied with age in the manner of the average diet of the Swedish population. The "best fit" calculated 4.8% lifetime average absorption of dietary Cd, 440 μg Cd/d at age 50, and a 12 year biological half-life for Cd to achieve the 200 μg Cd/g wet kidney cortex at age 45-50.

Other researchers have used different ways to express Cd-exposure information, thus complicating interpretation of results from these many sources. In the U.S., the Food and Drug Administration (FDA) has measured food Cd concentrations and average Cd ingestion (FDA, 1977). Food consumption was based on USDA's dietary intake survey; FDA, USDA, and EPA agreed to use a food consumption model based on teenage males (highest food consuming group) in a pesticide residue survey program. Thus, for the same food supply, a mean food Cd ingestion of 39 $\mu\text{g}/\text{day}$ from FDA corresponds to about 23 $\mu\text{g}/\text{day}$ intake at age 50 in Kjellstrom and Nordberg's (1978) model. Their model reflected 3430 cal/d for Swedish teenage males vs. 2045 cal/d for 50-year-old Swedish individuals (Fig. 4.32 and 4.34 in Friberg et al., 1974). Thus, the critical 440 μg Cd/day ingestion rate for 50-year-old individuals in Kjellstrom and Nordberg's (1978) model corresponds to approximately 738 μg Cd/d ingestion in U.S. teenage male diets. The present exposure is only 5.2% of the critical exposure ($23 \div 440$ or $39 \div 738$).

Chaney (1980) and Ryan et al. (1979) discuss difficulties in interpreting dose-response relationships for dietary Cd. Individuals vary widely in self-selected diet and dietary Cd (Yost, Miles, and Parsons, 1980), in Cd absorption rate (Flanagan et al., 1978), and in sensitivity to absorbed Cd. These phenomena are generally assumed to vary in a log-normal fashion in a population. Kjellstrom (1978) extended the 440 $\mu\text{g}/\text{d}$ model "critical" level to a population by arbitrarily using a geometric standard deviation of 2.35 based on studies of Cd in autopsy tissues (see Ryan et al., 1979 for details). However, Kjellstrom's (1978) model would require greater than 100% absorption of dietary Cd by the most sensitive individuals (see Figure 1 in Chaney, 1980).

The highest Cd absorption rate observed for humans is 25% reported by Flanagan et al. (1978) for a woman with mild anemia; Fe stress strongly increases Cd absorption. Several researchers (Chaney, 1980; Ryan et al., 1979) argued that it was unreasonable to extrapolate the 440 µg Cd/d "Average Human" model result to an assumed maximum sensitivity group with greater absorption of Cd than ever observed in humans. Further, individuals are unlikely to be in this greatest risk group for their whole lifetime.

Ryan et al. (1979) concluded that a 200 µg/d threshold model (based on average lifetime daily Cd intake) was more appropriate for dose-response considerations, as did the CEC (1978) workgroup. This value corresponds to about 10.6% lifetime Cd absorption rate for the most sensitive individuals $[4.8(440/200)]$.

Cadmium absorption by animals is strongly influenced by other dietary factors (Fox, 1976, 1979; Fox et al., 1978, 1979; Jacobs et al., 1978a, 1978b, 1978c; Flanagan et al., 1978; Welch, House, and Van Campen, 1978; Welch and House, 1980; Neathery and Miller, 1975; Kostial et al., 1979; Cousins, 1979; Kobayashi, 1978; Washko and Cousins, 1977). Iron status of the animal appears to be the most important control of %-absorption of Cd. Zinc status of the animal and dietary Zn level is the next most important factor, followed by dietary Ca. Protein and fiber in the diet and age of animal also influence Cd retention. These factors should allow a greater %-absorption rate for women than men. Women as a group showed greater Cd absorption (Flanagan et al., 1978), and women's kidney Cd exceeds men's in autopsy kidney studies.

Dietary interactions can thus influence bioavailability of Cd. Leafy and root vegetables which are enriched in Cd may also be a good dietary supply of Zn, Fe, and Ca. Leafy vegetables have been shown to provide bioavailable Fe and Zn (Welch, House, and Van Campen, 1977, 1978; Van Campen and Welch, 1980; Wien, Van Campen, and Rivers, 1975). Chaney (1980) suggested that for leafy and root vegetables grown on soils enriched in Cd from being fertilized by low Cd, low Cd:Zn sewage sludges comprise a separate scenario. In this case, consuming sufficient food Cd to pose a risk to susceptible individuals would result in increased dietary Fe, Zn, and Ca, thereby shifting the individual to a less susceptible population group.

Feeding studies have been conducted with sludge and with crops grown on sludge-fertilized soil. Ingestion of sludge Cd has been evaluated in ruminant and monogastric animals with most work done with cattle. When sludges with high Cd

and high Cd:Zn were fed, kidney Cd was significantly increased (Kienholz, 1980; Baxter, Johnson, and Kienholz, 1980; Hansen and Hinesly, 1979; Hinesly et al., 1979; Edds et al., 1980; Fitzgerald, 1980). However, when sludges with lower Cd and low Cd:Zn were fed, kidney Cd was not significantly increased (Decker et al., 1980; Kienholz, 1980; Baxter, Johnson, and Kienholz, 1980; Smith et al., 1977; Smith, Kiesling, and Sivinski, 1978; Edds et al., 1980; Smith, Kiesling, and Ray, 1979; Smith et al., 1980). Sludge Cd was less bioavailable to swine than equal Cd added as CdCl₂ (Osuna et al., 1979; Edds et al., 1980). Food products of animals are unchanged in Cd except for liver and kidney (e.g., Sharma et al., 1979). Kienholz (1980) noted that dietary interactions could avoid even this impact of sludge Cd. Thus, risk analysis for ingested sludge Cd requires evaluation of several factors other than dietary Cd concentration.

Similarly, risk analyses for ingestion of Cd in foods grown on Cd-enriched soils requires careful evaluation of factors other than Cd. Far too little research has been conducted to characterize bioavailability of food Cd. Further, very little of the completed research conforms with the experimental designs which Fox et al. (1978, 1979) and Fox (1976) indicated were needed to allow interpretation. Dietary Cd level should correspond to the range of nutritional relevance to humans. Intrinsically Cd labelled foods should be fed in the state ordinarily ingested by humans (e.g., fresh leafy vegetables). Nutritional status of the experimental diet should be adequate for all known essential factors or varied as part of the experiment. The feeding period should be of sufficient length to allow nutritional status of animals to be under control of experimental diet for the bulk of the experimental period. Several animal species should be studied. Bioavailability of Cd in a food or a sludge grown food can only be determined experimentally.

Tobacco is an especially high risk crop in terms of potential for Cd effects on humans. Among all crops studied to date, tobacco accumulates more Cd per unit soil Cd than any other (Chaney et al., 1978a; MacLean, 1976). Tobacco is normally grown on strongly acid soils to prevent crop loss from root diseases. This soil pH management leads to maximum Cd uptake under normal crop production conditions. In contrast, most other crops are best grown at pH 6.5 to 7. Tobacco is normally high in Cd compared to leaves of other crop plants, and high leaf Cd levels in some production areas are being studied (Frank et al., 1977; Westcott and Spincer, 1974). When tobacco is grown on sewage sludge-amended soils, crop Cd level can be increased from 1 to as high as 44 ppm Cd in dry leaves (Chaney et al., 1978a) with only 1 ppm soil Cd.

Cadmium in tobacco is an important source of Cd for humans. Individuals who smoke one pack of cigarettes per day have about 50% higher Cd in kidney cortex than non-smokers (Lewis et al., 1972; Elinder et al., 1976). About 15% (5-25%) of cigarette Cd enters the mainstream smoke (Szadkowski et al., 1969; Menden et al., 1972; Westcott and Spincer, 1974). Filters can remove much of this Cd and reduce Cd exposure of smokers (Westcott and Spincer, 1974; Franzke, Ruick, and Schmidt, 1977). Based on the potential of sludge-applied Cd to increase risk of chronic kidney disease in smokers if sludge were applied to tobacco cropland, EPA (1979) regulated and discouraged this practice.

Several food crops are of especial importance to evaluating Cd-risk for humans. While grains supply much Cd to individuals in the general population (Braude, Jelinek, and Corneliussen, 1975; Jelinek and Braude, 1978; Ryan et al., 1979), gardeners are unlikely to grow a significant portion of their food grains. Rather, individuals are likely to grow leafy and root vegetables, legume vegetables, garden fruits, and potatoes. If the Cd:Zn ratio of an acidic Cd-enriched garden soil is high, edible crop tissues of leafy, root, and legume vegetables, garden fruits, and potatoes can be greatly increased in Cd concentration with no injury to the crop and provide excessive bioavailable Cd. If the Cd:Zn ratio of an acidic Cd-enriched garden soil is low (< 0.010), these crops are not greatly increased in Cd when Zn phytotoxicity limits crop yield, and bioavailable Cd would be only slightly increased. The difference in risk from low Cd:Zn and high Cd:Zn gardens is due to: 1) Zn-phytotoxicity at low pH in the low Cd:Zn garden causing the gardener to add limestone which reduces crop Cd or have little yield (hence, reduced exposure), 2) interactions between Cd and Zn in plant uptake and translocation to edible plant tissues (Chaney, White, and Tienhoven, 1976; Chaney and Hornick, 1978); and 3) interactions in the diet which influence Cd bioavailability (Chaney, 1980).

It is much more difficult to evaluate Cd bioavailability from foods grown on waste-amended soils than from Cd-amended purified diets. Freeze-dried lettuce and chard grown on acidic soils amended with domestic sludge were fed at a high % of diet to mice or guinea pigs (Chaney et al., 1978b, 1978c). Although dietary Cd was increased by up to 5-fold by lettuce or chard grown on acidic, domestic sludge-amended soil, kidney Cd was not increased. In other studies with high Cd and/or higher Cd:Zn sludges, feeding sludge-grown crops has caused increased kidney Cd (Chaney et al., 1978b; Miller and Boswell, 1979; Bertrand et al., 1980; Williams, Shenk, and Baker 1978; Hinesley, Ziegler, and Tyler, 1976). Clearly, many more sludge-soil-plant-animal studies are

needed to characterize the bioavailability of Cd in crops grown on waste-amended soils. It seems very likely that factors besides background soil pH, and annual and cumulative Cd application will eventually have to be considered in setting allowed Cd loadings on land treatment sites (EPA, 1979, 1980b; Chaney, Hornick and Parr, 1980).

Much of the potential risk from Cd in waste-amended soils has now come under regulation, although these regulations do not have to be enforced for several more years. The highest risk case, application of sludges to gardens as fertilizers or soil conditioners, has not yet been regulated (Comptroller General, 1978; Chaney, Hornick and Parr, 1980). Further, pretreatment of Cd-bearing industrial wastes, segregation of waste streams, and avoidance of Cd use for non-critical applications offer great opportunity to avoid all Cd health effects (Dage et al., 1979; Gurnham et al., 1979; Chaney and Hundemann, 1979).

In the process of developing Federal Regulations for land application of sewage sludge (EPA, 1979), EPA prepared a "worst case" scenario relating sludge-applied soil Cd to potential for kidney dysfunction (EPA, 1979b). The worst case which may occur appears to be the acid garden case. Individuals in the U.S. do not grow their own food grain on acidic, Cd-enriched soils. Similarly, consumption of liver and kidney enriched in Cd from sludge utilization, is a minor source of dietary Cd.

Thus, the acidic garden scenario was used. It presumed that 1) the garden contains the full allowed Cd application, 5 kg/ha; 2) the garden is continuously acidic, about pH 5.5; 3) the gardener obtains 50% of his annual supply of garden vegetables from the acidic, sludge-amended garden, including potatoes, leafy, root, and legume vegetables, and garden fruits; 4) the individual eats these amounts of garden vegetables for 50 years from the acidic sludge-amended garden; and 5) the individual is part of the sensitive-to-cadmium portion of the population. Further, EPA relied on the FDA teenage male diet model, which supplies 39 μg Cd/day. They subtracted this 39 μg Cd/d from the 71 μg /d WHO-FAO (1972) provisional maximum daily Cd ingestion to obtain a maximum allowed increase due to sludge use. Others have noted that U.S. adult dietary Cd is about 20 μg /d (Ryan et al., 1982).

It appears now that several linked assumptions of EPA's acidic garden scenario may well be mutually exclusive, and provide excessive protection. First, individuals who grow 50% of their garden vegetables have such a large time and work investment in their gardens that they learn about the

effects of acid soils on yield of vegetable crops, and carefully manage soil pH at 6.5 to 7. Second, presuming that a low Cd, low Cd:Zn ratio sludge applied the soil Cd, and that soil pH declines slowly due to fertilizer use, phytotoxicity in sensitive crops will cause a "50% gardener" to learn about soil pH management and interrupt the necessary 50 year acid garden exposure. Third, vegetables supply microelements which counteract Zn, Fe, and Ca deficiencies; these deficiencies are the identified basis for sensitive individuals. Thus, consumption of the vegetables which comprise the minimal Cd risk to sensitive individuals may push them out of the sensitive population. Recall that increased Cd in "domestic" sludge grown chard and lettuce did not cause increase in kidney Cd (Chaney et al., 1978b, 1978c). In their discussion of Cd dose-response models, Ryan et al., (1982) concluded that U.S. sensitive individuals are protected at the 150 μg Cd/day level of exposure ($150/20 = 130 \mu\text{g}/\text{d}$ vs $71/39 = 32 \mu\text{g}/\text{d}$). Based on the above discussion, it seems clear that the EPA (1979, 1980b) limits are very protective of the worst recognized case when recommended low Cd sludges are managed by land treatment. As a result of these newer understandings discussed above, the regulatory and advisory Federal agencies developed a policy statement on utilization of sewage sludge on cropland for production of fruits and vegetables (EPA-FDA-USDA, 1981).

In summary, the "Soil-Plant Barrier" does not protect the food chain from excessive Cd. Unregulated application of Cd-bearing wastes can cause health effects in humans. Cadmium is not easily kept out of food crops; conversion of treated land to gardens is a worst case scenario upon which regulations to limit Cd applications were based (EPA, 1979a, 1980b). Recent research on gardens polluted with Cd by mining wastes or smelter emissions support the view that gardens can provide much Cd in locally grown foods to the family maintaining the garden for many years (Davies and Ginnever, 1979; Chaney et al., 1980. Unpublished.). Many aspects of the waste-soil-plant-animal food chain are not well established, and research is needed to avoid unnecessarily restrictive limits in the regulations.

Chromium--Chromium is not essential for plants (Huffman and Ataway, 1973). Chromium is essential for animals (Underwood, 1977; Mertz, 1969; NRC, 1980b). An organic chelated Cr^{+3} compound (Toepfer et al., 1977) is a cofactor in insulin hormone response controlling carbohydrate metabolism. Human diets are often deficient in this Cr compound, and some older humans presently experience Cr deficiency (NRC, 1980b; Underwood, 1977).

Chromium exists in two redox forms in nature: chromic (Cr^{3+}) and chromate (Cr^{6+}). Bartlett and Kimble (1976a) show an Eh-pH diagram for Cr in water. Chromium in soil solution is further decreased since chromic is strongly adsorbed and chelated by soils at all practical pH levels (Bartlett and Kimble, 1976a; Cary, Allaway, and Olson, 1977b; Grove and Ellis, 1980). Chromate is rapidly reduced to chromic in soils; reduction is more rapid in acidic soils (Bartlett and Kimble, 1976b; Cary, Allaway, and Olson, 1977b; Grove and Ellis, 1980; Bloomfield and Pruden, 1980).

Bartlett and James (1979) discovered that soluble chromic could be oxidized to chromate in soils and that air drying soils prevented this reaction. Although oxidation may be important in plant uptake of Cr, it is not yet clear that chromic oxidation is significant in the natural environment since chromic is so insoluble and strongly sorbed. Recent research has shown that freshly precipitated (less crystalline) MnO_2 oxidizes the chromic, producing chromate and manganous (Bartlett and James, 1979; Amacher and Baker, 1980; Slater and Reisenauer, 1979; Bartlett, 1979). Bloomfield and Pruden (1980) recently found that soils have substantial chromate adsorption capacity, using a method improved from that of Bartlett and James (1979).

Plant uptake of Cr to plant shoots is generally very limited. Even when soluble chromate is supplied, it is reduced to chromic in plant roots and kept there as chelates, precipitates, or adsorbed Cr. Chromate can be quite phytotoxic (Turner and Rust, 1971; Chapman, 1966; Gemmell, 1973; Breeze, 1973; Mortvedt and Giordano, 1975; Slater and Reisenauer, 1979). However, even under conditions of chromate phytotoxicity, plants contain <10 ppm Cr (normal plant shoots are <2 ppm Cr).

Because humans are often deficient in Cr, research has been conducted on methods to increase Cr in plants. Although chromate existence is more favorable at alkaline pH, adjusting soil pH had little effect. Repeated sub-phytotoxic additions of chromate to soils, and adding 1% Cr as freshly precipitated $\text{Cr}(\text{OH})_3$, did increase Cr in plant leaves, but not in grain or fruits (Cary, Allaway, and Olson, 1977a,b). Heating soils to 300°C to simulate effects of forest fires caused soil chromate to increase; corn grown in heated soil had greater Cr in roots than plants grown on unheated soils, but not in shoots (Hafez, Reisenauer, and Stout, 1979). Most plants growing on naturally high Cr serpentine soils have only normal levels of Cr (Cary, Allaway, and Olson, 1977b; Proctor and Woodell, 1975; Anderson, Meyer, and Mayer, 1973). However, some plants occurring naturally on these soils are tolerant of the low Ca status and high Ni and Cr.

Both endemic and ecotypic serpentine tolerant plant species include some Cr accumulators (Lyon et al., 1968, 1970, 1971; Wild, 1974; Shewry and Peterson, 1976).

Lyon, Peterson, and Brooks (1969) found that Leptospermum scoparium (a Cr accumulator) translocated Cr in xylem as chromate. However, Cr in roots and shoots was chromic (Lyon, Brooks, and Peterson, 1969); the major identifiable soluble Cr anionic chelate was trisoxalatochromium(III) in all tissues except xylem exudate. Shewry and Peterson (1974), Skeffington, Shewry, and Peterson (1976), and Lahouti and Peterson (1979) examined Cr uptake and translocation by barley. In contrast to the results with L. scoparium, chromate remained chromate in the roots; further, some chromic was oxidized to chromate by the roots, and the trisoxalatochromium(III) was not found in roots or shoots. Lahouti and Peterson (1979) found new evidence for trisoxalatochromium(III) in shoot and root extracts of several species supplied Cr^{3+} or Cr^{6+} . Chromate may limit plant growth on high Cr serpentine soils. Based on the study of Anderson, Meyer, and Mayer (1973), chromate in the displaced soil solution was thought to be too low to be toxic to any plants. However, this work used air-dried soils, and air-drying temporarily inhibits a soil's ability to oxidize chromic to chromate (Bartlett and James, 1979). Thus, the whole subject must be re-evaluated with soils not air-dried before studying.

The food chain is well protected from excess Cr by the "Soil-Plant Barrier." Animals tolerate high levels of insoluble Cr components in their diet (NCR, 1980b). Chromic oxide has actually been fed as a dietary marker for animals (Raleigh, Kartchner, and Rittenhouse, 1980; Dansky and Hill, 1952; NRC, 1980b; Underwood, 1977) and even humans (Kreula, 1947; Irwin and Crampton, 1951; Schurch, Lloyd and Crampton, 1950; Whitby and Lang, 1960). Recently, McLellan et al. (1978) showed that $^{51}\text{Cr}^{3+}$ mixed in a diet is an effective label to indicate when all (99.9% of ingested ^{51}Cr by 16 days) of a meal has finally transited the digestive system and been excreted. NRC (1980b) indicated that 3000 ppm Cr as insoluble Cr_2O_3 or 1000 ppm Cr as other chromic salts were tolerated by domestic animals. Because crop plants have such low Cr levels even when grown on soils very high in Cr, the food chain is protected against excess plant absorbed Cr. Animal ingestion of organic wastes rich in Cr appears to offer a similarly low hazard based on sewage sludge (Kienholz, 1980) and tannery sludge (Dilworth and Day, 1970; Knowlton et al., 1976; Waldrup et al., 1970) feeding studies. Hydrolyzed leather meal ($\leq 2.75\%$ Cr) is an approved feed ingredient (Anonymous, 1967).

Chromate has been found to be mutagenic (Petrilli and de

Flora, 1977) and carcinogenic, particularly if inhaled; humans and experimental animals exposed to chromate dusts and mists are quite susceptible to nasal cancer (Towill et al., 1978; NRC, 1980b). Chromate in feed has not caused similar cancer in experimental animals, and chromic in feed was not carcinogenic or mutagenic. Chromate in land-applied wastes is rapidly converted to chromic, greatly reducing the chance for a carcinogenic risk. In contrast, when chromate-rich inorganic wastes are placed on the land, chromate may remain for a long period (Breeze, 1973; Gemmell, 1973).

Land application of refuse compost, sewage sludge, tannery sludge, cooling tower blowdown, and sewage effluent can cause Cr in the surface soil to be greatly enriched. However, these practices have not yet been shown to affect Cr in soil below the tilled zone, and do not increase plant Cr after the first crop year (Mortvedt and Giordano, 1975; El-Bassam, Poelstra, and Frissel, 1975; Taylor, 1980; Grove and Ellis, 1980; Kick and Braun, 1977; Silva and Beghi, 1978; Cunningham, Keeney, and Ryan, 1975; Dowdy et al., 1979, 1980; Dowdy and Ham, 1977). Gemmell (1974) and Breeze (1973) found that sewage sludge and refuse compost were very effective in reducing chromate toxicity in smelter wastes.

In summary, Cr in organic wastes is very unlikely to cause food chain problems because animals tolerate high levels of insoluble Cr compounds in diets, and plants do not absorb and translocate high levels of Cr to edible plant tissues even when soils are greatly enriched in Cr.

Cobalt--Cobalt is essential for plants which are dependent on N fixed by nodule bacteria (See Loneragen, 1975). Cobalt is essential for animals; ruminants can use plant Co to make vitamin B₁₂, while monogastric animals require B₁₂ (Underwood, 1977; NRC, 1980b).

Cobalt in soils is strongly sorbed and even co-precipitated with the manganese oxides (McKenzie, 1972). Availability of soil Co to plants is controlled by two major factors, MnO₂ in soil and soil pH. Because MnO₂ adsorbs Co so strongly, soils high in MnO₂ often produce forages with deficient Co for ruminants. Cobalt fertilizers can not be successfully used to increase plant Co on these soils (Adams et al., 1969; Loneragen, 1975). Poorly drained soils generally produce plants having higher Co concentration than nearby well drained soils, apparently because MnO₂ surfaces can not effectively adsorb Co under these conditions (Kubota, Lemon, and Allaway, 1963; Allaway, 1968; Loneragen, 1975). Cobalt deficiency of livestock is found on a limited number of soil types in the U.S. (Kubota and Lazar, 1958; Kubota and Allaway, 1972).

Soil pH is very important in Co uptake and phytotoxicity. More acidic soils sorb Co less strongly, allowing plants to absorb it (Adriano, Delaney, and Paine, 1977; Fujimoto and Sherman, 1950; Wallace and Mueller, 1973). Cobalt reactions are similar to those of Ni in soils and plants except for the strong effect of soil MnO₂ on Co uptake.

Phytotoxicity from soil Co results in plants containing 50-100 ppm when foliar symptoms are apparent (Vergnano and Hunter, 1952; Hunter and Vergnano, 1953; Wallace and Mueller, 1973; Austenfeld, 1979; Wallace, Alexander, and Chaudry, 1977). Only a few plant species accumulate Co above the 100 ppm which causes severe phytotoxicity. Hyperaccumulators of Co have been found which contain over 1% Co in dry leaves (Yamagata and Murakami, 1958; Kubota, Lazar, and Beeson, 1960; Brooks, 1977; Brooks, McCleave, and Malaise, 1977). Co-tolerant non-accumulators have also been found (Hogan and Rauser, 1979). The physiological mechanisms of Co, Ni, and Zn phytotoxicity have been studied in some detail by Rauser and co-workers. They recently showed that phytotoxicity inhibited pumping sugars from mesophyll cells into the phloem and veins, severely altering energy transport to rapidly growing tissues (Rauser and Samarakoon, 1980).

Cobalt phytotoxicity has not been of practical importance. Cobalt is seldom used by itself in industrial processes. Pinkerton et al. (1981) studied phytotoxicity and excessive plant Co on a Co-contaminated petroleum landfarm where the soil was Co-enriched by catalyst wastes. Uses of some industrial enzymes require Co as a co-factor. Soils naturally rich in Co are richer in Ni, and Ni phytotoxicity usually dominates (Anderson, Meyer, and Mayer, 1973).

Cobalt toxicity in livestock has not been reported under field conditions. Experimentally, adding over 10 ppm Co to the diet of cattle and sheep has caused Co toxicity (NRC, 1980b; Becker and Smith, 1951; Keener, Baldwin, and Percival, 1951; Keener et al., 1949; Dunn, Ely, and Huffman, 1952; MacLaren, Johnston, and Voss, 1964).

Humans experienced Co toxicity in a few cities when local breweries added Co to beer to stabilize the foam. Heavy beer drinkers died from sudden heart attacks (Anonymous, 1968). Research has not fully clarified this disease. Monogastric animals, not drinking alcoholic beverages, appear to tolerate about 50 ppm Co in their diet (NCR, 1980b; Burch, Williams, and Sullivan, 1973; Huck and Clawson, 1976).

Based on these findings with soil, plants, and animals, Co should be able to cause toxicity to ruminants grazing

healthy Co-rich forages. Monogastric animals should not be injured because grain and fruit tissues are only somewhat Co-enriched when Co-phytotoxicity causes visual crop damage. Individuals consuming large amounts of leafy vegetables grown on Co-toxic soils may be at risk. Because none of these risks have been observed in nature, they should be studied to learn whether even the worst case can cause Co-toxicity in any animals.

In summary, the food-chain appears not to be protected from Co toxicity by the "Soil-Plant Barrier." Research is needed on all aspects of Co in waste-soil-plant-animal systems to determine whether this is an actual risk even under worst case conditions.

Copper--Copper is an essential element for plants and animals. Phytotoxicity occurs in most plants at about 25-40 mg Cu/kg dry foliage (Chaney and Giordano, 1977; Page, 1974; Chapman, 1966; Walsh, Erhardt, and Seibel, 1972). Copper toxicity to sensitive sheep and cattle occurs at 25-100 mg Cu/kg dry diet (NRC, 1980b). Cu toxicity in animals can be counteracted by increased dietary Zn, Cd, Fe, or Mo (Suttle and Mills, 1966; Mills, 1978; McGhee, Creger, and Couch, 1965; Standish et al., 1971; Mills and Daigarno, 1972; Campbell and Mills, 1979; Bremner, 1979). Accidental Cu toxicity in sheep has resulted from feeding pig rations high in Cu; high levels of Cu are added to promote gains in the absence of antibiotics (Baker, 1974; Davis, 1974). Mills (1978), Schwarz, and Kirchgessner (1978), L'Estrange (1979), and Bremner, Young, and Mills (1976) suggested that increasing Zn in these pig rations would reduce the consequences of feeding them to sheep.

Crops with 25-40 ppm Cu could be grown on strongly acid soils rich in Cu from sewage sludge; these crops would have high Zn and normal Fe. Thus, Cu toxicity to even sensitive ruminants from crops fertilized with domestic sludges appears extremely unlikely. Wastes unusually high in only Cu might cause toxicity through ingestion of the waste or soil. For the case of direct ingestion of "Domestic" sludges, the interactions with other dietary and sludge constituents (Fe, Zn, fiber, sulfide) was so pronounced that liver Cu of cattle was depleted rather than increased to toxic levels (Decker et al., 1980; Kienholz, 1980); for high Cu sludges, liver Cu may rise (Bertrand et al., 1980; Johnson et al., 1981). It may be possible to have Cu toxicity expressed as induced-Mo-deficiency if forages are marginal or deficient in Mo, and the sludge is rich in Cu and S, but low in Mo.

As noted in the "pathways" and "interactions" sections above, the potential for effects from land application of

high Cu swine manure has caused concern. As in the sewage sludge case (Chaney, 1980), earlier research indicated that sheep would be easily poisoned by applied Cu but field studies found no injury to sheep grazing high Cu swine manure fertilized pastures. These manures contain 500 to 1500 mg Cu/kg dry weight (Aumaitre, 1981). Studies showed extensive plant contamination from adhering manure, and enrichment of the surface organic layer with manure Cu (e.g. McGrath, 1981). Even under the conditions of multi-year practical manure application, sheep were not injured (Bremner, 1981; Poole, 1981; Unwin, 1981). Although manure Cu is "bioavailable" in controlled research studies, the presence of other minerals (Zn, Fe), and of ingested surface soil reduce the practical bioavailable Cu to non-toxic exposures. Authorities do recommend a waiting period after spray application to reduce Cu and pathogen exposure.

A recent study by Gupta and Haeni (1981) illustrates a principle underlying all heavy metal reactions with soils, especially more strongly adsorbed elements such as Cu. When Cu was mixed with sewage sludge to comprise varied proportions of the Cu-saturation capacity, and then applied to sand at varied Cu levels, excessive plant uptake and phytotoxicity was easily caused by sludge of higher Cu-saturation levels and CuSO_4 , but not by lower Cu sludge. Repeated application of high Cu manure causes Cu accumulation in the soil; although great concern has been voiced regarding Cu phytotoxicity (Lexmond, 1981; Lexmond and DeHaan, 1980), corn Cu has been affected little (Mullens, 1982). These results are corroborated by research on Cu toxicity from sewage sludge (Webber et al., 1981; Davis, 1981a; Beckett, 1981). Soil and manure in the diet of sheep greatly increases the Cu-sorption capacity of the diet, and can induce Cu-deficiency in diets of normal Cu content (Suttle, Allaway, and Thornton, 1975). Thus risk to sensitive livestock from Cu in wastes is much lower than expected, and eventual Cu-phytotoxicity from excessive soil Cu accumulation is likely the dominant risk.

It is likely that land treatment of industrial wastes rich in Cu but very low in Zn and Mo could lead to Cu toxicity in grazing ruminants; Underwood (1977, p. 96) noted this result on Cu rich, low Mo Australian soils. Monogastric animals are much more tolerant of dietary Cu than ruminants. Further, Cu is generally much lower in fruits and grain than leaves when soils are high in Cu. Thus, humans are at no risk from sludge applied Cu even in the worst case acid garden scenario.

Fluorine--Fluorine is not an essential element for plants; it has been shown to be essential for animals through

feedings of highly purified diets low in F. Practical diets provide adequate F.

Plant uptake of F is strongly controlled by precipitation of inorganic F compounds in soil; CaF_2 formation had been presumed, but the exact chemical species controlling F-activity has not been demonstrated (could be fluoroapatite). Plant F is increased by F additions to soil only where soil Ca activity is very low (strongly acid soils) (Chapman, 1966; Prince et al., 1949). Sewage sludges are not rich in F, and sludge use has not been reported to increase crop F unless extremely F contaminated sludge was used (Davis, 1980). Phosphate fertilizers have added F to cropland (Gilpin and Johnson, 1980). The "Soil-Plant Barrier" is very effective in limiting impact of soil F via plant uptake; monogastric animals are fully protected from soil F.

Direct ingestion of F rich sludges or soil could affect animals depending on the chemical forms of F present (Davis, 1981). Kienholz et al. (1979) observed significant increases in bone F in cattle fed sewage sludge. Sludge F should be CaF_2 or fluoroapatite, forms of low bioavailability (NRC, 1980b; Underwood, 1977) compared to NaF. Most fluorosis in domestic animals results from high F water supplies. Another important cause of fluorosis is industrial air-borne F pollution which contaminates forages allowing direct ingestion of F. Industrial wastes rich in F are poor candidates for surface application on land treatment sites which will be used as pastures for cattle or sheep.

Iron--Iron is an essential element for plants and animals. Phytotoxicity of Fe is not an agronomic problem except when rice is grown on some reduced soils (Foy, Chaney, and White, 1978). Leaves of most crops contain 30-300 mg Fe/kg dry weight. Fertilizing with sludges does not cause foliar Fe to rise above these normal levels; sludge can increase foliar Fe concentration from deficient levels (30-40 ppm in chlorotic leaves) to normal, and may be a valuable Fe fertilizer (McClaslin and Rodriguez, 1978; McClaslin and Sivinski, 1979).

Plant Fe can reach unusually high levels due to interactions with other plant micronutrients (Olsen, 1972). Deficiencies of Cu (DeKock, Cheshire and Hall, 1971), Mn, or Zn (Ambler and Brown, 1969; Warnock, 1970) can cause foliar Fe to exceed 1000 ppm. Excessive Fe in leaves is stored as phytoferritin (Seckbach, 1968, 1969).

The levels noted above are for leaves free of soil. Soil dust (<1% dry weight) on leaves can supply more total Fe than internal plant Fe. Trampled forages become "soiled"

(Healy, Rankin, and Watts, 1974). Spray-applied sludges may greatly increase Fe in/on forages (Chaney and Lloyd, 1979), allowing forage Fe to exceed even 1% dry weight (Decker et al., 1980). This external Fe (from anaerobic sludge) can injure domestic animals, while internal plant Fe has shown no evidence of toxicity to animals.

Animals tolerate higher levels of Fe than normally occur in feedstuffs (NRC, 1980b). However, chronic Fe toxicity is complex, and toxicity of sludge-borne Fe depends on many interactions. Dietary Fe interacts strongly with Cu and Zn; 1000 ppm Fe added to a forage diet reduced Cu in sheep and cattle liver (Standish et al., 1969, 1971; Standish and Ammerman, 1971; Grun et al., 1978). On low Cu diets, Fe toxicity is expressed as an Fe-induced Cu-deficiency. However, when sewage sludge supplies the excessive Fe, it also supplies Cu (which would tend to correct Cu deficiency) and Zn, Cd, S, Mo, and fiber which could further interfere with Cu utilization (Anke, 1973; Bremner, 1979).

The chemical form of Fe influences Fe bioavailability. Iron in FeSO_4 is 3 to 5 times more available to cattle than Fe in ferric oxide (Ammerman et al., 1967). Much of the Fe in anaerobically digested sludge is in the ferrous form; this quickly oxidizes as the sludge becomes aerobic. Iron in soils (and sludges on the soil surface) should have different bioavailability depending on the degree of crystallinity of the ferric oxides present.

Iron toxicity was suspected in cattle grazing tall fescue pastures sprayed with a digested sewage sludge containing 11% Fe (Decker et al., 1980). When lower Fe anaerobic sludges, or when sludge composts are applied, iron toxicity did not result (Decker et al., 1980; Bertrand et al., 1981). That sludge was low in Cu. Liver Cu was at marginal or deficient levels in the cattle on sludge treatments. Liver Cu has been low in most studies of sludge feeding (Kienholz, 1980). In two studies, with sludge Cu at 1000 ppm, the cattle showed Cu balance or a slight increase in liver Cu (Kienholz, 1980; Baxter, Johnson, and Kienholz, 1980; Johnson et al., 1981; Bertrand et al., 1980).

Thus, high Fe wastes which are low in Cu can promote Fe-induced Cu-deficiency and high Fe accumulation in liver, spleen, and intestine. Even the erosion of cartilage in joints of cattle (Decker et al., 1980) may be due to a severe Cu deficiency. Zinc-induced Cu deficiency in horses (Willoughby et al., 1972; Willoughby and Oyaert, 1973; Gunson et al., 1982) caused erosion of cartilage in joints very similar to that observed in cattle grazing pastures fertilized with high Fe sludge.

Industrial sludges and other wastes high in Fe may cause Fe-induced Cu-deficiency if they are surface applied to pasture land. Zinc and Mo in the waste can also contribute to the toxicity, and Cu in the waste can counteract it. Supplemental Cu may be needed for ruminants grazing pastures where high Fe wastes remain on the soil surface.

Lead-- Lead is not essential for either plants or animals. Phytotoxicity due to Pb has been observed only under unusual conditions of phosphate deficiency. Because sewage sludges contain high amounts of P, Pb in domestic sludge has not caused increased plant Pb. Plants do not ordinarily translocate high amounts of Pb to their shoots (< 5 ppm) because an insoluble Pb-phosphate is formed in the roots. However, high foliage Pb has been reported for grasses growing on infertile, strongly acidic, Pb-mine spoils (Johnson, McNeilly, and Putwain, 1977; Johnson and Proctor, 1977).

Lead toxicity to animals occurs at about 30 mg Pb/kg diet (NRC, 1980b); Pb interacts strongly with dietary Fe, Ca, Zn, P, fiber, etc. (Mahaffey, 1978; Mahaffey and Vanderveen, 1979; Levander, 1979). Thus, animals appear to be protected from excess Pb in crops grown on land treatment sites. A seasonal increase in foliar Pb occurs in forages growing during mild winters (Mitchell and Reith, 1966). This seasonal increase was not exaggerated in crops grown on soils enriched in Pb by sewage sludge (Haye et al., 1976).

As noted above, consumption of soil can comprise a risk for elements not readily accumulated by plants. Consumption of soils with naturally high Pb concentrations and mine wastes has caused Pb toxicity in domestic livestock (Egan and O'Cuill, 1970; Harbourn, McCrea, and Watkinson, 1968; Edwards and Clay, 1977; Thornton and Kinniburgh, 1978). Ingestion of domestic sewage sludges has not caused Pb toxicity, probably because sludge Fe, P, Ca, etc. counteract Pb absorption (Kienholz, 1980). Industrial wastes high in Pb comprise a very different case than domestic sewage sludge. Conversion of land treatment sites to uses allowing children to ingest soil should require consideration of whether this exposure could allow Pb poisoning if the soils are too high in Pb.

As noted earlier, children ingest soil and dust by 1) a deliberate practice of consuming non-food items, called "pica", and 2) normal hand-to-mouth play activities and mouthing of toys etc. (Lepow et al., 1975; Sayre et al., 1974; Roels et al., 1980). High Pb soils can be carried into homes on dusty clothing and shoes (e.g. Archer and Barratt, 1976), thereby causing housedust to become rich in Pb (Jordan and Hogan, 1975). Several research programs have shown that

soil Pb and housedust Pb contribute to Pb exposure of children (Angle and McIntire, 1979; Charney, Sayre, and Coulter, 1979; Galke et al., 1977; Roels et al., 1980, Barltrop et al., 1974; Hammond et al., 1980). Paint Pb, air Pb, soil Pb, and housedust Pb comprise a multiple source model for Pb exposure of children.

Perhaps the clearest example of the possibility of human health effects from inadvertent ingestion of high Pb house-dust is found in recent cases in which children of Pb-industry workers experienced excessive blood Pb. The only identifiable source of Pb was the industrial dusts carried into the house on the workers' clothing and shoes (Baker et al., 1977; Giguere et al., 1977; Rice et al., 1978; Fergusson, Hibbard, and Ting, 1981).

Soil Pb can only cause excessive blood Pb if it is at least somewhat bioavailable to humans. Studies have shown that soil Pb is largely bioavailable to rats (Dacre and Ter Haar, 1977; Stara et al., 1973), but that soil properties can reduce Pb bioavailability (Chaney et al., 1980). At the pH of the stomach of monogastric animals, soil Pb is quite soluble (Day et al., 1979). Table 9 shows results from a study of the bioavailability of soil Pb to rats. Although soil properties do reduce apparent risk from soil Pb, these Pb rich garden soils would add to Pb absorption risk to children. Garden soils are enriched in Pb (in descending order of impact) from exterior and interior paint; application of ashes, sludges, and pesticides; and automotive emissions (Davies, 1978; Preer et al., 1980; Spittler and Feder, 1979; Ter Harr and Aronow, 1974). Many research questions must be addressed to allow setting of maximum acceptable levels for soil Pb.

Recent research indicates a different health risk from Pb than those traditionally relied on in developing regulations, the effects on heme synthesis and frank lead encephalopathy. This new clinical result of low level lead exposure is neuro-behavioral impairment (Needleman et al., 1979; Needleman, 1980; Silbergeld and Hruska, 1980; David et al., 1978). Lower IQ and school achievement, and problem classroom behavior appear in populations of Pb-exposed children whose exposure was not great enough to require chelation therapy (60 g Pb/dL blood), or source identification (30 to 40 g Pb/dL). A recent National Research Council review considered the potential importance of soil and dust ingestion in Pb poisoning and low level lead exposure of children (NRC, 1980a).

Molybdenum--Molybdenum is essential for both plants and animals. Molybdenum is present in soils and plants as

TABLE 9. EFFECT OF SOIL ON AVAILABILITY OF Pb TO RATS, AND
BIOAVAILABILITY OF Pb IN URBAN GARDEN SOILS ^{1/}

Diet ^{2/}	Tibia Ash mg/tibia	Pb in Tibia mg/kg tibia ash \pm S.E.
Basal	102	0.3 \pm 0.3 e ^{3/}
Basal + 5% Soil	101	0.0 \pm e
Basal + PbOAc	92	247. \pm 10.1 a
Basal + PbOAc + 5% Soil	105	130. \pm 29.5 bc
706 ppm Pb Soil	98	40.0 \pm 6.1 de
995 ppm Pb Soil	96	108. \pm 26.3 c
1078 ppm Pb Soil	100	37.1 \pm 7.3 de
1265 ppm Pb Soil	107	53.6 \pm 7.4 d
10240 ppm Pb Soil	92	173. \pm 21.8 b

^{1/} Levander, O. A., R. L. Chaney, S. O. Welsh, C. H. Gifford, and H. W. Mielke (unpublished results, USDA, Beltsville, MD).

^{2/} Fed to Fisher rats for 30 days. A purified casein-based complete diet was fed; Pb acetate and garden soils were added to supply 50 mg Pb/kg dry diet.

^{3/} Means followed by the same letter are not significantly different (P<.05) according to Duncan's Multiple Range Test.

anionic molybdate. This causes Mo to differ markedly in its reactions with soils and plants from those of the potentially toxic cations (e.g. Zn^{2+}) for which liming to alkaline pH reduces plant uptake (see also review by Jarrell, Page, and Elsewi, 1980). Soils adsorb Mo more strongly under more acidic conditions; inorganic compounds of Mo have not been identified in soils (Vlek and Lindsay, 1977a). The strong Mo sorption at low soil pH holds Mo against leaching and reduces plant Mo uptake. Alkaline soil pH weakens soil sorption of Mo, promoting plant uptake of Mo, and allowing Mo to leach through the root zone with leaching water. Sorption of Mo is further decreased by reducing conditions (low E_h). Molybdenum uptake is greatest in alkaline, poorly drained soils with Mo enrichment (Kubota, 1977). The chemical or biological basis for greater Mo concentration in plants growing on poorly drained soils remains unclear. It has been suggested that a higher percentage of plant roots in the surface soil, greater Mo solubility (lower sorption) in

reduced soils, or reduced plant biomass diluting absorbed Mo may explain these higher concentrations (Allaway, 1977c; Kubota et al., 1961; Kubota, Lemon, and Allaway, 1963; Vlek and Lindsay, 1977b).

Plants tolerate very high levels of Mo, and translocate Mo to edible plant tissues. Legume crops accumulate substantially more Mo than do grasses (Chapman, 1966; Allaway, 1977c; Jensen and Lesperance, 1971; Kubota, 1977). Vegetable crops are also Mo accumulators (Hornick, Baker and Guss, 1977; Gupta, Chipman, and Mackay, 1978).

Ruminant animals are especially susceptible to Mo toxicity (molybdenosis) because Mo interacts to induce a Cu deficiency (Mills, et al, 1978; Underwood, 1977). Dietary Mo interacts also with sulfate (increased sulfate competitively reduces Mo absorption), Mn, Zn, Fe, tungstate, sulfur-containing amino acids, etc. Dietary sulfate and Cu are the primary factors interacting with excessive dietary Mo. Normal forages contain 0.1 to 3.0 ppm Mo (dry weight basis). Levels over 10 ppm Mo are generally high enough to cause molybdenosis; lower levels can cause molybdenosis depending on dietary Cu availability. Plants grown on poorly drained, alkaline, Mo enriched soils can exceed 100 ppm Mo, far surpassing the levels necessary for molybdenosis (10 ppm). Industrial air pollution from Mo-smelters, oil refineries and steel mills have caused molybdenosis (Hornick, Baker and Guss, 1977; Alary et al., 1981; Gardner and Hall-Patch, 1962, 1968; Buxton and Allcroft, 1955; Parker and Rose, 1955). It is clear that the "Soil-Plant Barrier" does not protect the ruminant animal food-chain from excessive soil Mo.

A few soils in the U.S. have naturally high Mo levels, and cause molybdenosis in cattle and sheep (Kubota, 1977). Soil and crop management can reduce the problem; draining the area and growing grasses rather than legumes reduces potential molybdenosis considerably. Land treatment sites for Mo-rich wastes can be managed to remove the Mo from the surface soil before ruminants are allowed to graze the area; drainage and crop selection are important. Adequate or high copper in crops and surface soil reduces Mo risk. Animals can be supplemented with Cu by injection, or salt licks or feed supplements containing Cu.

Sewage sludges are very seldom high in Mo (median = ca 10 ppm). Historically, sludge use has not been reported to cause molybdenosis in ruminants through either plant uptake or direct ingestion of sludge. High Mo sludges do exist, and would be a cause for concern (Table 5) (Lahann, 1976; Sterritt and Lester, 1981). Sludge Cu would counteract any effects of considerable amounts of Mo in most ingested

sludges. Fly ash is richer in Mo than sludges and has been evaluated as a Mo-fertilizer; fly ash Mo is about as available to plants as Na molybdate (Doran and Martens, 1972). Molybdenosis could result where high rates of fly ash are applied on alkaline pastures (Gutenmann et al., 1979).

Monogastric animals are protected from excess soil Mo by the "Soil-Plant Barrier"; Mo concentration in grain is lower than in leaves, monogastric animals are more tolerant of Mo than ruminants, and monogastric animals are seldom fed grain crops grown only on a restricted area of land. It is conceivable (but very unlikely) that humans could be at some risk of molybdenosis by consuming large amounts of garden crops grown on high Mo alkaline soils which had previously been used for land treatment of Mo rich wastes. Sites managed at lower soil pH to avoid excessive crop Mo can subsequently cause molybdenosis after limestone is applied (Hornick, Baker and Guss, 1977).

Nicker--Nickel is an essential element for animals and probably is for plants (Polacco, 1977; Welch, 1981). Phytotoxicity causes visible symptoms (interveinal chlorosis of young leaves) at about 50-100 mg/kg dry leaves. These levels are phytotoxic for grasses, legumes, and leafy vegetables (Chapman, 1966; Chaney et al., 1978a; Hunter and Vergnano, 1952; Roth, Wallihan and Sharpless, 1971; Halstead, Finn, and MacLean, 1969; Anderson, Meyer, and Mayer, 1973). Some plants are very tolerant of soil and plant Ni and are Ni-accumulators; plants tolerating over 1000 mg Ni/kg dry leaves have been labelled hyperaccumulators (Brooks et al., 1979; Jaffre et al., 1976; Wild, 1970; Morrison, Brooks and Reeves, 1980). These Ni-accumulator species are rare and are not reported among crop plants.

Nickel toxicity in domestic animals occurs at 50-100 mg Ni/kg feed where Ni is added as soluble salts (NRC, 1980b). This range of Ni tolerance in livestock overlaps the range of Ni present in plants at phytotoxicity. However, when NiCO_3 was added to cattle diets, no toxicity was observed at 250 ppm Ni (O'Dell et al., 1970). Greater tolerance in animals could also occur to Ni in green forage or hay grown on land treatment sites. Little study has been done with Ni bioavailability in foods or feeds grown to contain high levels of Ni. Alexander et al. (1979) found no health effect or Ni bioaccumulation in voles fed sludge-fertilized soybeans containing 30 ppm Ni; this is the Ni level in soybean grain when yield is significantly reduced.

Based on these results, it seems very unlikely that Ni toxicity would occur in ruminants grazing Ni phytotoxic forages on worst case acidic, high Ni land treatment sites.

The availability of ingested soil Ni has not been reported. Grain and vegetable crops do not accumulate Ni to levels which would injure monogastric animals. Although wildlife might be affected by Ni-rich sludges on the soil surface, they would not be by Ni in crops.

Selenium--Selenium is not essential for plants, but is for animals. The forms of Se in soil depend on soil pH and redox (Geering et al., 1968). At equilibrium, most soil Se should be elemental Se. Selenate additions are weakly adsorbed by soils; selenite is strongly sorbed on hydrous iron oxide surfaces; elemental Se is quite inert compared to elemental S, but some oxidation occurs; selenide is readily oxidized in soils (Allaway, 1977a; Carter, Brown and Robbins, 1969; Cary and Allaway, 1969). Plant residues can supply seleno-amino acids to soil (Olson and Moxon, 1939). Some Se in soil and plants is converted to dimethylselenide and volatilized (Lewis, Johnson and Broyer, 1974).

Selenate in soils is readily absorbed by plants, while selenite is not as plant available since it is sorbed strongly by soil. After plant uptake, selenite is more easily converted to seleno-amino acids than selenate. Elemental Se is so inert that it will not supply enough soluble Se to plants to correct Se deficiency in animals. In the year that elemental Se (or flyash) is applied to soil, plant Se is somewhat increased. Selenite is a useful slow-release Se fertilizer which corrects Se deficiency of animals for a number of years while not allowing plant Se to reach acutely toxic levels (>3 ppm) during the year of application (Cary and Allaway, 1973; Carter, Brown and Robbins, 1969). Neutral soil pH favors both plant uptake and leaching of Se through soils.

Once Se is absorbed by plants, it is freely translocated to edible plant tissues, including grain (Anderson et al., 1961; Allaway, 1968, 1977a). Selenium follows the sulfate pathway in uptake, translocation, and metabolism (Asher, Butler, and Peterson, 1977). Plant species differ widely in relative Se uptake (Hamilton and Beath, 1963; Allaway, 1968). Although most plant species convert only a small fraction of absorbed Se to seleno-amino acids, a few convert Se extensively. These species are endemic to high Se soils (Shrift and Virupaksha, 1965; Trelease and Trelease, 1939; Anderson et al., 1961; Trelease, 1945). When these plants die, seleno-amino acids are returned to the soil, greatly increasing the amount of plant available Se in the soil (Olson and Moxon, 1939).

Small areas of the Great Plains have naturally Se toxic soils (Kubota et al., 1967; Kubota and Allaway, 1972;

Anderson et al., 1961). Domestic livestock were poisoned by the high Se crops. Acute poisoning can result from ingestion of plants which convert Se to seleno-amino acids (e.g., Astragalus sp.) (Allaway, 1968; Anderson et al., 1961). Chronic poisoning can also result from ingestion of Se-accumulating normal forages and grains grown on the Se-rich soils. Humans were not shown to suffer serious health effects in these areas, although mild Se effects were observed (Anderson et al., 1961); medical science was not well developed at that time and renewed research might detect human health effects. These natural Se poisoning incidents clearly show that the "Soil-Plant Barrier" fails to protect animals from excessive soil Se (Allaway, 1968; Anderson et al., 1961; Trelease, 1945).

Sewage sludges are usually low in Se and this has prevented toxicity from sludge-borne Se. Sludge ingestion research has also shown no Se impacts (Kienholz, 1980). However, fly ash from coal burning power plants can be quite rich in Se when Western coals are burned (Furr et al., 1977). Crops grown on fly ash amended soils are high in Se, and animals can obtain excessive Se by this route (Furr et al., 1975, 1977; Gutenmann et al., 1976). On the other hand, fly ash can be used at lower application rates as a Se-fertilizer to amend the large areas of land in the U.S. which yield crops with Se too low to satisfy the needs of animals (< 0.1 ppm) (Stoewsand, Gutenmann, and Lisk, 1978; Combs, Barrows, and Swader, 1980, Gutenmann et al., 1979). Similarly, fly ash can be a Se-feed supplement (Furr et al., 1978b; Hogue et al., 1980).

In summary, the food chain is not protected from excessive soil Se. Land treatment of wastes high in Se will require management designed to avoid food-chain impacts of soil Se (e.g., use at low rates as a Se fertilizer). Selenium toxic land in South Dakota was purchased by the Federal Government to prevent or minimize Se-poisoning risks (Anderson et al., 1961). Use of selected management practices has allowed some productive use of these lands.

Tin--Tin is not essential for plants; one study suggested Sn was essential for rats fed a highly purified diet, but it is not yet generally agreed that Sn is essential for animals (NRC, 1980b; Underwood, 1977).

Tin forms very insoluble minerals in soils (SnO_2), and this appears to prevent plants from accumulating much Sn regardless of soil pH. Studies by Romney, Wallace and Alexander (1975) and Kick and Warnusz (1972) found that, for addition of soluble Sn salts to soils, soil of very low pH may allow some phytotoxicity; for soil pH near neutral, 500

ppm Sn had no effect on several crop species, and did not increase foliar Sn. Several biogeochemical studies of Sn, and studies of Sn in plants growing on Sn mine wastes, showed very little uptake of Sn by plants even when soil Sn was quite high (Millman, 1957; Peterson et al., 1976). The latter authors found a few plant species which had increased foliar Sn when found growing on Sn mine wastes. The levels were only 20 ppm, far below levels tolerated by animals.

Tin has very low toxicity when mixed with practical diets. Rats tolerate several hundred ppm with no effects; at higher dietary Sn, supplemental Fe and Cu counteract effects of Sn (deGroot, 1973; deGroot, Feron, and Til, 1973). Tin-contaminated fruit juices had little effect on animals (Benoy, Hooper, and Schneider, 1971). Studies of the bio-availability of soil Sn or effects of ingesting Sn-rich soils have not been reported; it appears that this would be very unlikely to affect grazing animals.

Sewage sludges contain low levels of Sn. No effects of sludge Sn on animals, or residues of Sn in animals fed sludge have been reported.

Thus, the food chain is protected from excess Sn by the "Soil-Plant Barrier." Tin in industrial wastes should have little influence on plants or animals when applied to a land treatment site.

Vanadium--Vanadium is essential for some algae, but apparently not for higher plants (Welch and Huffman, 1973). Vanadium is essential for animals, although the requirement is low. Practical diets supply adequate V for domestic livestock (NRC, 1980b; Underwood, 1977).

Vanadium is a constituent of many petroleum materials, coals, and some rock phosphates. Some industrial wastes are enriched in V from these sources.

Little is known about forms of V in soils. Many redox species of V are possible, but forms in soil have not been reported. Soils naturally contain 30-100 ppm V (and higher near ore deposits), but only a small fraction of this is extractable. Crops growing on most soils contain low V, less than 1 ppm dry weight (Welch and Cary, 1975). Supplying soluble forms of V in nutrient solution did increase V in shoots of most plants; however, V was poorly translocated from roots to shoots (Welch and Huffman, 1973; Wallace, Alexander, and Chaudhry, 1977). Tyler (1976) suggested that V could inhibit soil enzymes, at least when soluble V is added. Soluble V can be phytotoxic, but this may be environmentally irrelevant depending on soil reactions of V.

So little is known about V reactions in soil and plant uptake of V from soil that it is difficult to evaluate risks from land treatment/application of industrial wastes rich in V. The NRC (1980b) indicated that ruminants would chronically tolerate 50 ppm V, and monogastric animals 10 ppm V; forage V would be lower than 10 ppm V when V is phytotoxic. One study on V-accumulator plants growing on V-mineralized soils indicated plant foliage could reach 150 ppm V under unusual circumstances (Cannon, 1963, 1964). The bioavailability of V in forages and grains remains ill-defined.

As noted above, little was known about soil-plant relationships for V. Furr et al. (1977) applied fly ash from 15 sources at 7% in a neutral pH soil. Vanadium in the ash varied from 68 to 442 ppm, and V in the cabbage was only 0.02 to 0.4 ppm. Further study with other crops and one fly ash showed no change in crop V due to fly ash application. Sewage sludge also caused no change in plant V (Chaney et al., 1978c).

In summary, the "Soil-Plant Barrier" appears to protect the food chain from excess soil V. So little research has been done on V that no conclusion is possible.

Zinc--Zinc is an essential element for plants and animals. Phytotoxicity (ca. 25% yield reduction) occurs in most plants at about 500 mg Zn/kg dry foliage (Chapman, 1966; Boawn, 1971; Boawn and Rasmussen, 1971; Walsh et al., 1972b). Leafy vegetables such as chard and spinach may be more tolerant of foliar Zn; chard does not show phytotoxicity in acid soils until foliar Zn is about 1500 mg/dry kg (Baxter, Chaney, and Kinlaw, 1974). Zn toxicity to domestic livestock occurs at 300 to 1000 mg/kg dry diet (NRC, 1980b). This Zn toxicity appears to result from Zn-induced Cu deficiency (Grant-Frost and Underwood, 1958; Lee and Matrone, 1969; Campbell and Mills, 1979; Bremner, 1979; Gunson et al., 1982; Bremner and Campbell, 1980). Sheep are more sensitive to excessive dietary Zn if Cu in the feed is marginal to deficient (Campbell and Mills, 1979).

Several factors influence risk of soil Zn. Crop uptake of Zn is strongly reduced as soil pH increases. Forage crops are poor accumulators of Zn compared to vegetables and crop plants. Forage crops grown on sewage sludge amended soil would have normal to somewhat enriched Cu concentration to counteract the Zn; however, industrial wastes high in Zn but low in Cu would comprise a greater Zn risk to the food chain than sewage sludge.

Ruminant animals could consume Zn rich sludges from the

soil surface. For alkaline soils, sludge and soil ingestion could supply more Zn than the forage crops grown on the amended soil; for acidic soils, crop uptake would be the predominant Zn source. For animals consuming domestic sewage sludge, dietary Cu and Fe would be substantially increased along with Zn and would counteract the risk of Zn toxicity. For high Zn sludges or industrial wastes, these protective factors might not be increased.

Forage crops comprise the worst case for evaluation of excess soil Zn. Under conditions of high Zn supply, grain and fruit contain lower Zn concentrations than leaves. Research by Ott et al. (1966), Campbell and Mills (1979), L'Estrange (1979), and Bremner, Young, and Mills (1976) indicate that crop uptake of Zn is very unlikely to cause Zn poisoning of cattle or sheep. Although humans could consume appreciable amounts of high Zn leafy vegetables (acid soils; phytotoxicity), it is very unlikely that Zn toxicity would occur in humans in even this worst case. Leafy vegetables supply appreciable Cu and Fe, especially if grown on sludge-amended soils, and these counteract the Zn risk. Individuals are unable to consume high Zn leafy vegetables as the bulk of their diet the whole year. Many humans presently consume low or deficient amounts of Zn (Hambridge et al., 1972); increased food Zn would be beneficial in many cases.

Wildlife comprise a greater risk case than do domestic animals because wildlife could chronically consume Zn-phytotoxic foliage as most of their diet. It seems likely that high Zn sludges and industrial wastes could cause adverse health effects (due to Zn-induced Cu-deficiency) in wildlife such as that resulting from Zn smelters (Gunson et al., 1982; Bremner and Campbell, 1980).

In summary, land application/treatment of sewage sludges and industrial wastes is very unlikely to cause Zn toxicity in domestic livestock or humans even under worst case conditions. Wastes unusually high in Zn but low in Cu may cause Zn toxicity to animals if mismanaged.

Potential Food-chain Impacts of Toxic Organic Compounds Applied in Industrial Wastes

Introduction--

Animals can be exposed to toxic organic compounds (TO's) present in wastes by the pathways described above: 1) direct ingestion of wastes, wastes adhering to forages, wastes lying on the soil surface, or soil treated with wastes; 2) ingestion of plant tissues which are increased in TO content after plant uptake or volatilization from the soil to the

plant; or 3) consumption of animal products enriched in TO by other routes. The chemical and physical properties of a TO control its adsorption by soil, volatilization, plant uptake and translocation, biodegradation (in soil, plant or animal), and accumulation in animal tissues. Because each TO is chemically and pharmacologically unique, each compound will have its unique behavior in waste-soil-plant-animal systems (Fries, 1982; Majeta and Clark, 1981; Dacre, 1980). Another chapter in this book describes the fate of organic compounds in land-applied wastes, including sorption by soils, plant uptake and translocation to shoots, volatilization from soils and contamination of plant shoots or edible roots, and chemical-, photo-, and bio-degradation.

Although much research has been conducted on insecticides, fungicides, and herbicides, insufficient information is available to assess food chain risk of waste-borne TO's. Environmentally relevant research on waste-borne TO's is quite limited even among pesticides. Very little is known about fate and potential for food-chain effects of industrial TO wastes and byproducts that may be considered for application to land treatment sites.

Thus, this subsection will describe the processes which influence movement of TO's in waste-soil-plant-animal food chains. This should illustrate the research needs for assessing potential impacts of a TO or a TO-enriched waste. PCB's in sewage sludge will provide a particularly relevant example, as regulations were developed based on the available research (EPA, 1979a).

Bioavailability of Ingested Waste-borne Toxic Organics--

Lipophilic toxic organics in ingested sludges and soil are bioavailable. DDT and lindane in ingested soil were absorbed by sheep and stored in their fat (Harrison, Mol, and Healy, 1970; Healy, Mol, and Rudman, 1969; Collett and Harrison, 1968). PCB's and other compounds in ingested sludge were absorbed and stored in fat of cattle (Kienholz, 1980; Baxter, Johnson, and Kienholz, 1980; Fitzgerald, 1978, 1980), cow's milk (Bergh and Peoples, 1977), and fat of swine (Hansen et al., 1981). In general, PCB residues in fat reached levels 5-fold higher than in dry feed.

Based on these studies and basic research on bioaccumulation of PCB's, Fries (1982) concluded that PCB's should not exceed 2.0 mg/kg dry sludge if milk cows are to be allowed to graze pastures under worst-case conditions which allow 14% sludge in their diet. This was based on a biomagnification from diet to milk fat of 5-fold, and FDA tolerances of 1.5 mg PCB/kg milk fat (FDA, 1979). Forages grown on soils

containing PCB's have PCB residues about 0.1 that of the soil, or lower. Good management practices (delay grazing for 30 days after surface application of sludge, and supply feed concentrates during periods of low forage availability) reduce sludge ingestion so that 10 ppm PCB's could be allowed in sludge surface applied at 10 metric tons/ha/yr. Injection of sludge below the soil surface would further reduce exposure.

A seldom considered concentration step involves soil fauna. Earthworms accumulate Cd (Helmke et al., 1979; Beyer, Chaney, and Mulhern, 1982), and lipophilic toxic organics. Beyer and Gish (1980) noted substantial residues of DDT, dieldrin, and heptachlor in earthworms many years post application. Birds and shrews consume appreciable earthworm biomass and are thereby exposed to Cd and pesticides. More study is needed to assess the importance of this unusual foodchain pathway in relation to land treatment of industrial wastes and potential effects on wildlife.

Plant "Uptake" of Toxic Organics in the Soil--

Toxic organics can enter edible parts of plants by two processes: 1) uptake from the soil solution, with translocation from roots to shoots, or 2) adsorption by roots or shoots of TO's volatilized from the soil. "Systemic" acting pesticides are applied to the soil, absorbed and translocated by the plant, and act to protect the plant leaves. These compounds are quite water soluble and would probably not appear in industrial wastewater treatment sludges at appreciable levels. Some systemic TO's are prohibited from use on food crops (other than seed protectants) since residues of the compound or its metabolites on or in food may be unacceptable. The EPA-approved label for each compound lists acceptable uses.

The lipophilic halogenated pesticides represent the case for water insoluble compounds which are largely sorbed by plants from the soil air or the pesticide-enriched air near the soil surface. Beall and Nash (1971) developed a method to discriminate between movement of a TO through the plant vascular system (uptake-translocation) vs. vapor phase movement. They found soybean shoots were contaminated by soil-applied dieldrin, endrin, and heptachlor largely by uptake-translocation. Vapor transport predominated for DDT, and was equal to uptake-translocation for endrin. Using this method, Fries and Marrow (1981) found PCB's reached shoots via vapor transport, while the less volatile PBB's did not contaminate plant shoots by either process (Chou et al., 1978; Jacobs, Chou and Tiedje, 1976). Suzuki et al. (1977) found that PCB's with a low number of chlorines could be absorbed and translocated at low rates by soybean seedlings

from sand treated with high levels of PCB's.

Root crops are especially susceptible to contamination by the vapor-transport route. Carrots have a lipid-rich epidermal layer (the "peel") which serves as a sink for volatile lipophilic TO's. Depending on the water solubility and vapor pressure of the individual compound, it may reside nearly exclusively in the peel layer of carrots, or penetrate the storage root several mm (Lichtenstein, Myrdal, and Schulz, 1964, 1965; Jacobs, Chou, and Tiedje, 1976; Lichtenstein and Schulz, 1965; Iwata and Gunther, 1976; Iwata, Gunther, and Westlake, 1974; Fox, Chisholm, and Stewart, 1964; Landrigan et al., 1978).

Carrot cultivars differ in uptake, and in peel vs. pulp distribution of the chlorinated hydrocarbon pesticides endrin and heptachlor (Lichtenstein, Myrdal, and Schulz, 1965; Hermanson, Anderson, and Gunther, 1970). Other root crops (sugar beet, onion, turnip, rutabaga) are much less effective in accumulating lipophilic TO's in their edible roots, possibly because the surface of the peel is lower in lipids (Moza, et al., 1979; Moza, Wiesgerber, and Klein, 1976; Fox, Chisholm, and Stewart, 1964; Chou, et al., 1978; Lichtenstein and Schulz, 1965).

The level of chlorinated hydrocarbon in carrots is sharply reduced by increased organic matter in soil. The increased organic matter adsorbs the TO's and keeps them from being released to the soil solution or soil air (Filonow, Jacobs, and Mortland, 1976; Weber and Mrozek, 1979; Chou, et al., 1978; Streck, et al., 1981). Added sewage sludge increased the ability of soils to adsorb PCB's (Fairbanks and O'Connor, 1980). At some low level of PCB's in sludge, the increased sorption capacity may fully counteract the increased PCB's.

Assessing risk from environmental exposure to PCB's, or other TO's is difficult. PCB's and other persistent chlorinated hydrocarbons seldom occur at excessive levels in present municipal sludges (Sprague et al., 1981). The residue of PCB's in waste products is depleted of the relatively more volatile lower chlorinated compounds, but most research is conducted with the commercial mixture. It is clear that plant contamination by the higher chlorinated compounds is much less than for the lower chlorinated ones at equal soil levels (Iwata and Gunther, 1976; Suzuki et al., 1977; Moza, Weisgerber, and Klein, 1976; Moza et al., 1979; Fries and Marrow, 1981). Recently, research has begun with the individual ¹⁴C-labelled PCB's; risk evaluation should focus on the 5, 6, and more highly chlorinated compounds which remain in wastes and soils. Assuming peeling of

carrots, the only significant exposure to these higher chlorinated PCB's is to grazing ruminants through soil ingestion. One field research study with a "domestic" sludge (contained 0.93 ppm PCB's) evaluated PCB uptake by carrots; Lee et al. (1980) were unable to detect PCB's in the carrots even though they applied sludge at 224 mt/ha and immediately grew the crops.

Another research effort centered on assessing risk from polycyclic aromatic hydrocarbons (PAH's). Some PAH's are carcinogenic (e.g., benzo(a)pyrene). Researchers found PAH's in composted municipal refuse, and that carrots roots (but not mushrooms) accumulated many PAH's from compost-amended soils (Muller, 1976; Linne and Martens, 1978; Wagner and Siddiqi, 1971; Siegfried, 1975; Siegfried and Muller, 1978; Neudecker, 1978; Ellwardt, 1977; Borneff et al., 1973). The level of 3,4-benzopyrene in carrot roots declined with successive cropping of compost amended soil. Multi-generation feeding studies of control and compost grown carrots found no risk to rats (Neudecker, 1978). Most of the PAH's in human diets result from deposition on plant foliage; root vegetables are a minor source.

Many other carcinogenic or toxic compounds may be present in wastes, and contaminate the food chain through plant uptake, volatile contamination of crop root or shoots, or soil ingestion. Very little information is available on these. Nitrosamines have been found in sewage wastes (Yoneyama, 1981; Green et al., 1981) and are accumulated from nutrient solution and soil by plants (Brewer, Draper, and Wey, 1980; Dean-Raymond and Alexander, 1976). However, nitrosamines appear to be rapidly degraded in soils and plants. Research on N-nitrosodimethylamine and N-nitrosodiethylamine found rapid degradation in soil; plant uptake did occur but these compounds were rapidly degraded there (Dressel, 1976a, 1976b). Traces of nitrosamines are found in nitroaniline based herbicides. These compounds are rapidly degraded and no detectable nitrosamine was found in soybean shoots (Kearney et al., 1980a). An IUPAC committee assessed the environmental consequences of these trace nitrosamines, and found no risk to the food chain (Kearney, et al., 1980b).

Aflatoxin comprises another useful example on fate of toxic organic compounds. Aflatoxin contaminated agricultural wastes are usually tilled into cropland. Aflatoxin is readily decomposed or transformed to nonextractable forms in soil, although detectable aflatoxin remained for about 50 days when 2 ppm was applied (Angle and Wagner, 1980). If present in nutrient solution or freshly amended soil, aflatoxin can be absorbed by corn or lettuce (Mertz et al., 1980; 1981). Thus, although it is possible for plants to

absorb aflatoxin from aflatoxin amended land treatment sites, none would remain after closure and little would remain at the time of crop growth after preparing the soil for seeding.

Bioassay techniques for plant residues of soil-borne TO's include 1) field studies, 2) controlled pot studies, 3) vapor barrier pot studies, and 4) small pot intensive uptake (many plants to observe maximum possible uptake) techniques. Results from growing many plants in a small volume of pesticide treated soil (Fuhremann and Lichtenstein, 1980) provide valuable information on possible pathways of TO movement. However, little information obtained is relevant to actual environmental exposures.

Land treatment appears to be an effective method for destruction of mutagens present in sludges. Sewage sludge, feces, and some crop residues contain mutagenic activity (Hopke et al., 1982). Donnelly and Brown (1981), and Brown, Donnelly, and Scott (1982), have characterized reduction in concentration of mutagens during land treatment of petroleum refinery and other industrial sludges. Angle and Wagner (1980) reported biodegradation of aflatoxin, a potent mutagen, when it was added to soil. These studies indicate that mutagens in land-applied sludge should be rapidly degraded. Recently Babich et al. (1981) have voiced concern about TO's in land-applied sewage sludge. These concerns seem to rely on mismanagement of land treatment sites, and presume very high (unlawful under EPA, 1979) application rates followed by immediate cropping with food crops (usually considered prohibited under a 18 month waiting period to prevent pathogen contamination of foods). Boyd (1981) recently grew 4 vegetables (snapbeans, beets, cabbage, and squash) on a soil amended with 112 mt/ha sludge from Syracuse, N.Y.; this industrially contaminated sludge was applied in the Fall, and crops grown the next season. The edible portion of the sludge-grown and control crops were fed to rats at 25% of their diet. Mutagen assays were conducted on the crops and the rat urine; liver enzyme changes were followed; and alpha-fetoprotein (indicates pre-neoplastic transformations) was assayed. Weight gain was comparable from control and sludge-grown crops. No evidence of change in alpha-fetoprotein was observed in rats consuming the 4 sludge-grown vegetables. The liver mixed-function-oxidase enzymes (aminopyrine-N-demethylase and p-nitroanisole-O-demethylase) were affected by type of crop, but no additional changes were observed due to growing the vegetables on sludge-amended soils. No ultrastructural abnormalities were observed in rat liver cells as a consequence of sludge-grown vegetables. Rat urine may have shown increased amounts of mutagens when the urine extract from rats fed sludge-grown crops was activated with mammalian microsomes. The extracts

of control and sludge-grown vegetables did not show significant "sludge effects" in normal or activated assays. Thus, although this topic has received little study to date, land treatment appears to provide sufficient biodegradation and adsorption to protect the food-chain from mutagenic compounds present in sludges applied to land under well managed programs. Food crops would not be grown during active land treatment periods.

Land treatment sites can be managed to avoid all unacceptable effects on the food-chain from waste-borne TO's. Wastes can be injected below the soil surface. Mechanically harvesting fresh forages or feed grain crops avoids soil contamination of food chain. Crops can be returned to the treatment site soil until plant absorbable TO's no longer reach unacceptable concentrations. Knowledge of the biodegradation and transport route for compounds in industrial wastes is required to prepare hazardous waste land treatment site management and closure plans (EPA, 1980b). And, if necessary, waste streams can be segregated and/or pretreatment used to remove TO's which are not acceptable in wastes subjected to land treatment.

Summary and Research Needs

Pathways to and potential effects on the food chain of macro- and microelements, and toxic organic compounds in wastes applied on land treatment sites are considered in detail. Wastes usually provide enough N, P, or K to be used as fertilizers. Wastes may cause nutrient imbalance if applied at excessive rates, or if all required nutrients are not supplied by the waste. Excess K (with or without adequate Mg) can cause magnesium deficiency (grass tetany) in cattle and sheep when wastes are used to produce forage grasses on poorly-drained soils. Management to avoid grass tetany is always needed, but wastes with high K/Mg require careful soil-crop-animal management.

Microelements can be placed into several groups based on their potential to cause health effects in livestock and humans. Waste-borne toxic chemicals can enter the food chain in 1) ingested wastes, wastes adhering to forages, or waste-amended soil, or 2) in plants which have increased levels of the toxic chemical when grown on waste-amended soil. Some waste-borne elements are unable to injure animals even when the waste is ingested (e.g., Ti, Cr⁺³, Zr, Si, Sn, Au, Ag), either because animals tolerate high exposures or the element is bound very strongly by the ingested soil or waste. Other chemicals can injure animals which ingest the waste or soil, but not when animals ingest plants grown on the amended soil (Fe, Pb, Ni, Zn, Cu, Be, As and bioaccumulated toxic organic

compounds), because phytotoxicity kills the plant before the metal concentration in the plant reaches toxic levels for the animal. On the other hand, risk may result from ingestion of forage crops containing phytotoxic levels of Co or excessive non-phytotoxic levels of Se, Mo, or Cd. Cumulative applications of only a few elements (Cd, Pb) have to be restricted to protect humans from the worst-case situations. These include 1) the long-term vegetable garden use scenario (chronic Cd-injury to kidney), or 2) the inadvertent soil ingestion scenario (Pb poisoning of children). If land treatment sites were not allowed to be converted to normal unregulated land use patterns until toxic organic compounds were degraded, management practices which avoided adverse food-chain effects could be developed for nearly any organic waste. Under those conditions it may be wise to avoid land treating on one site wastes which contain cationic toxic elements (Zn, Cd) best managed in alkaline soils and anionic toxic elements (Mo, Se) best managed in acidic soils.

Research Needs--

Some microelements have been insufficiently studied to provide adequate waste-soil-plant-animal management information. Too little is known about plant tolerance, plant uptake in relation to tolerance, and/or bioavailability of intrinsic plant Co to animals. Bioavailability information is needed for high levels of Zn, Cd, and Mn in vegetable crops. Bioavailability of microelements in ingested waste-amended soils has not been extensively studied. For Pb, this pathway is of overriding importance. It is also of interest, for Fe, As, Se, Zn, and Cu. Further research in this area is also needed for Zn, Cu, Ni, and Mn since few phytotoxicity studies have been conducted in the field. These are often present at substantial levels in wastes. Also, interactions among microelements, wastes, soils, plants, and animals need further study to develop management practices which prevent adverse effects on the food chain regardless of land use after closure.

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UTILIZATION OF MUNICIPAL WASTEWATER AND SLUDGES ON LAND — METALS

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INTRODUCTION

The 1972 amendments to the Water Quality Act, which would spur the construction of advanced wastewater treatment facilities and greatly increase the production of municipal sewage sludge in the U.S. were one year old when university researchers, representatives of the Federal agencies and others met at the University of Illinois to develop a coordinated program for research on land application of sewage sludge to land. Individual workgroups identified research needs and priorities on a number of questions, including metals. The dramatic increase in research on land application of sewage sludge in the following decade has helped to provide answers to some of these questions, while, at the same time, raising new issues and identifying new problems. In that same period, Federal, State and local agencies have attempted to formulate guidelines and regulations for the safe utilization and disposal of sewage sludges on land.

The purpose of this paper is to examine the various issues regarding the transmission of sludge-borne metals through the soil/plant/water system and its impact on livestock and human health. This paper is not intended as a comprehensive literature review of metals, a task beyond the scope of this report. It will examine, however, advancements made in the last ten years in our knowledge of the fate of sludge-borne metals when applied to land, and will also discuss the evolution of a regulatory approach to protect the food chain from toxic levels of metals. The reader who comes to this subject with little or no previous background is encouraged to consult a number of excellent reviews which have appeared in the last decade (Sommers, 1980; CAST 1976, 1980; Chaney 1980, 1983a, 1983b; Chaney and Giordano, 1977; Page, 1974; Baker and Chesnin, 1976; Leeper, 1978; Ryan et al., 1982; Walsh et al., 1976).

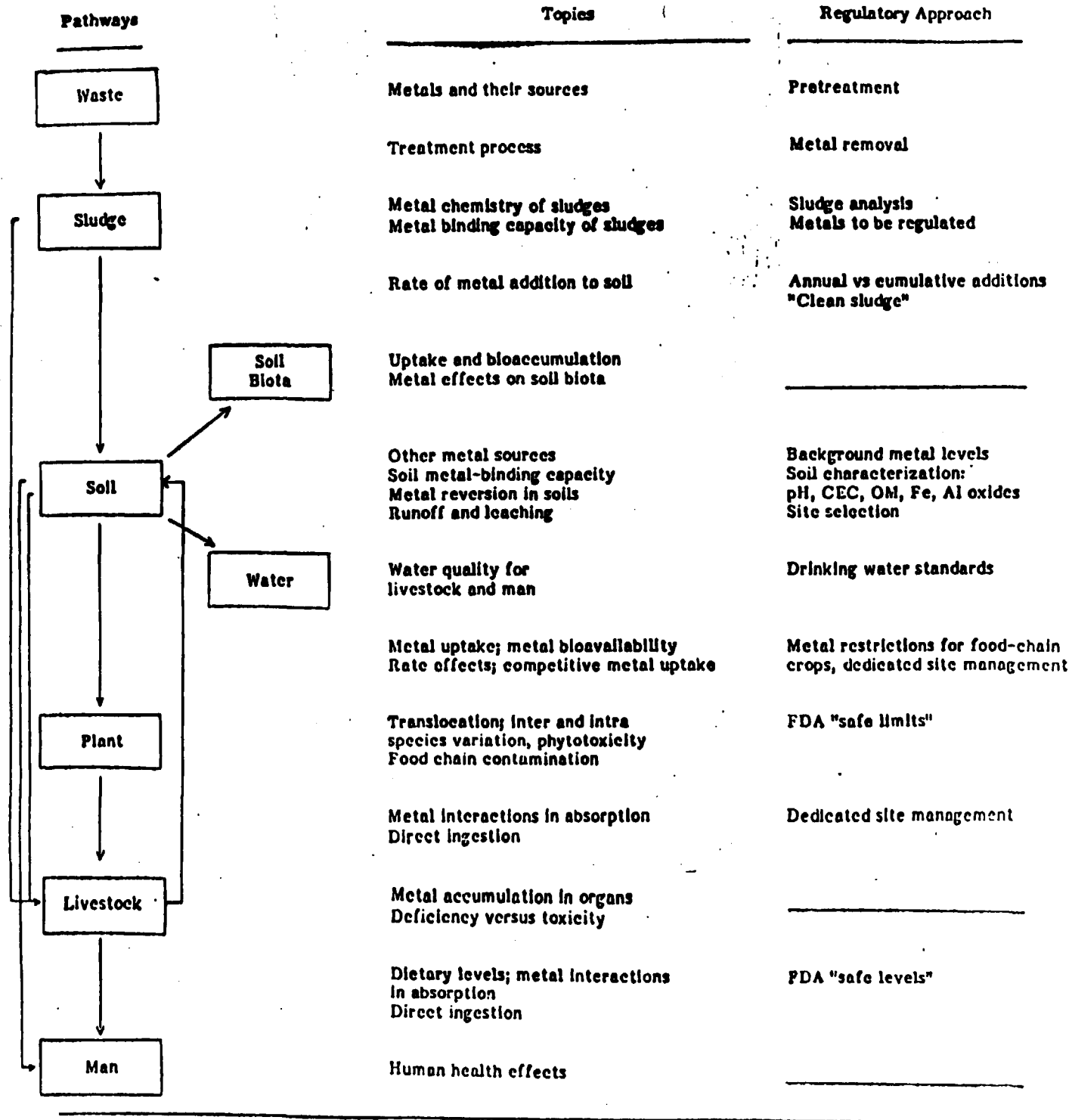
As Figure 1 shows, this paper will examine the transmission of metals from their sources, through the sludge treatment process, into the soil and through the plant and animal systems. Major issues listed in 1973 will be addressed and new research problems identified in 1983 will also be discussed. Present and potential regulatory approaches will also be identified.

METALS IN SLUDGE

METALS OF CONCERN

The 1973 Conference workshop group on Toxic Chemicals identified the following elements as being of primary concern because of either phytotoxicity or potential hazards to animals and man: Cd, Pb, Hg, As, Se, Zn, Cu, and Ni and indicated that, of these, Cd, Pb, Hg, As, Se and Zn should receive the highest priority because of their potential to contaminate the animal and human food chain. At the same conference, Chaney (1973) identified Cd, Cu and Zn as posing the greatest threat to animal and human health through plant accumulation.

Figure 1. Schematic of the biogeochemical trace element system as discussed in this paper.



The first report of the Council for Agricultural Science and Technology (CAST, 1976) identified Cd, Cu, Ni, Zn and Mo as the elements with the greatest potential to accumulate in plants and pose a hazard to plants, animals and humans. Pb, Hg, As, Se were not considered hazardous because "they either have low solubility in slightly acid or neutral, well-aerated soils or, as with selenium, are present in such small amounts that the concentration is low in soils." In addition, B was not considered hazardous in non-irrigated regions, but could be phytotoxic to sensitive crops at hot-water soluble concentrations > 1 mg/g soil. Molybdenum was included in the 1976 CAST report because the authors felt that "Mo may accumulate in plants at concentrations sufficient to cause molybdenosis in ruminant animals without prior warning from plant behavior." By 1977, cadmium was receiving considerable attention as a food chain contaminant. This was based on the extensive work by Japanese and European scientists (Ryan et al., 1982) and the growing awareness that Cd could readily accumulate in crops at concentrations which could increase the dietary intake of the metal without causing crop phytotoxicity. Shortly thereafter, the Federal government (EPA, 1979a) published interim final regulations for the control of Cd entry into the food chain via land application of sewage sludges. These regulations will be discussed in more detail later in the paper, but they dramatically increased the focus on Cd and decreased the attention being paid to potential problems from metal phytotoxicity.

By 1980, Chaney had introduced the term "Soil-Plant Barrier" in assessing the risks to the plant-animal-human system from toxic elements. Chaney (1983b) states that the Barrier protects the food chain when one or more of the following processes limit trace element transmission: 1) insolubility in the soil prevents uptake, 2) immobility of an element in fibrous roots prevents translocation to edible plant tissues or 3) phytotoxicity of the element occurs at concentrations of the element in edible plant tissues below that injurious to animals. Chaney (1983b) lists Cd, Se and Mo as elements which can escape the soil-plant barrier and adds Be and Co as metals which may also escape the barrier but are primarily added to soil in industrial wastes. As discussed later, the soil-plant barrier can be circumvented when animals directly ingest soil, sludge or vegetation on which soil or sludge particles adhere.

OTHER METAL SOURCES

Although widespread application of sewage sludges to land may provide the most ubiquitous source of metal additions to soil, there are other sources which can pose local problems. These include trace amounts of Cd in phosphate fertilizers (Mulla et al., 1980; Williams and David 1973, 1976), contaminated soils in the vicinity of smelters (Hutchinson and Whitby, 1974; Lagerwerff and Brower 1974), mine tailings (Benson et al., 1981; Robinson et al., 1947) and localized high natural concentrations of specific metals (Lund et al., 1981). While these may have local significance, their impact on the total metal burden to man is probably low. In many cases, food chain crops are not grown in the vicinity of these sources, and phytotoxicity greatly reduces the economic viability of these areas for crop production.

AMOUNTS

By 1973, results of extensive monitoring of metals in sludges were available from the U.S., Canada and Europe. Large variations in the concentrations of

metals were found. The distributions were skewed towards high concentrations (Dean and Smith, 1973) and arithmetic means overestimated the average metal concentrations of most municipal sludges. Dean and Smith (1973) and, more recently, Sommers (1977) have suggested using median metal concentrations as measures of average contents of municipal sludges, and these median values have been considered by some to represent reasonably attainable background levels in sludges after pretreatment to remove known sources. Table I gives median concentrations of the major metals found in sludges (Chaney, 1983b). These values are similar to values reported by Page (1974) for treatment plants in the U.S., Canada and Europe. Page (1974) also reported that metal concentrations in sludge were relatively unaffected by the sludge process used.

The 1973 Conference attendees agreed that pretreatment could reduce metal concentrations in sludges, but there was no agreement as to the level to which concentrations could be reduced. Metals from copper drains and galvanized plumbing were expected to maintain fairly high background levels of some metals, especially in soft water areas (levels were not specified). The lack of a comprehensive pretreatment program in the U.S. since 1973 makes it difficult to answer that question. National statistics are also difficult to obtain since many treatment plants have only recently begun to routinely analyze sludge for metals (Forster et al., 1981). However, examination of individual pretreatment programs reveal that metal concentrations can be drastically reduced. A pretreatment program at the City of Defiance, Ohio sewage treatment plant greatly reduced Cd and Ni levels in its sludge (Miller and Logan, 1979). Concentrations after pretreatment were similar to median values reported by Sommers (1977) for cities in the North Central U.S. Philadelphia, PA, Baltimore, MD, Washington, DC, and Ft. Collins, CO have achieved median metal sludges through pretreatment.

FORMS AND BIOAVAILABILITY

Speakers at the 1973 Conference did not address the question of forms of metals in sewage sludges, and a search of the literature prior to that time reveals very little research on the subject. Dean and Smith (1973) in their paper from the Conference state that "...organic matter in sludge complexes heavy metals...", but this is the only reference made to the metal chemistry of sludges. Surprisingly, characterization of metal forms in sludges was not identified by the conferees as a research need. A year later, Page (1974) reported that "as far as the author is concerned, no data are available on the chemical forms of trace elements which occur in sewage sludges." As recently as 1977, Chaney and Giordano (1977) indicated that "the chemical species of the individual metals present is not known."

Since that time, however, there has been considerable progress in the characterization of metal forms in sludges. Fractionation is one method of characterization. Gould and Genetelli (1975) used elutriation and filtration to separate sludge into four fractions: particulate, supracolloidal, colloidal and soluble. More than 90% of the metals were in the particulate fraction (> 100 mm diameter). Hayes and Theis (1978) developed a fractionation scheme which employed elutriation and filtration as well as acid and EDTA extraction of the particulates to give the following fractions: soluble, precipitated (insoluble), intracellular, and extracellular (adsorbed to the sludge biomass). These two schemes are primarily physical and do not characterize the chemical forms of the metals in sludge. Stover et al. (1976) presented a fractionation scheme which

TABLE 1. RANGES AND MEDIAN CONCENTRATIONS OF TRACE ELEMENTS IN DRY DIGESTED SEWAGE SLUDGES (Chaney, 1983b).

Element	Reported Range		Median
	Minimum	Maximum	
<hr/>			
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μg/g dry sludge			
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As	1.1	230	10
Cd	1	3,410	10
Co	11.3	2,490	30
Cu	84	17,000	800
Cr	10	99,000	500
F	80	33,500	260
Fe	1000	154,000	17,000
Hg	0.6	56	6
Mn	32	9,870	260
Mo	0.1	214	4
Ni	2	5,300	80
Pb	13	26,000	500
Sn	2.6	329	14
Se	1.7	17.2	5
Zn	101	49,000	1,700

partitioned metals into: exchangeable, adsorbed, organically bound, carbonate and residual. The residual fraction was uncharacterized, but would include such metal solid-phases as sulfide and phosphate. Silviera and Sommers (1977) sequentially extracted soil with 1M KNO_3 , 0.005M DTPA and 1M HNO_3 and found that metal extracted was generally proportional to the total content of the metal in the sludge. Distributions between the fractions for a given metal varied between sludges. In general, nitric acid extracted > 50% of the metal. Holtzclaw et al. (1978) extracted highly organic sludge-soil mixtures from sewage lagoons with 0.5N NaOH and fractionated the extracted metals into humic acid, fulvic acid and precipitable fractions. Fe, Al and Zn were generally associated with the precipitable fraction, while almost all of the copper was in the humic acid fraction. Cd and Zn were in the precipitable and fulvic acid fractions. The authors concluded from these results that Cd, Ni and Zn would tend to be more mobile in soil than Cu.

The bioavailability of sludge-borne metals will depend on those processes operating within the sludge which control metal activity in solution and the competing processes operating in the soil. Sludges are a sink as well as a source of metal, and some sludges may retain metals much more strongly than others. As Corey et al. (1981) have pointed out, the specific metal sorption capacity of a sludge may exceed the soil's affinity for the metal, and the bioavailability of the metal will be determined by the chemical characteristics of the sludge rather than the soil. If this is so, the present regulatory approach which considers only the total amount of metal added to soil and the soil's untreated background metal-binding capacity (e.g. cation exchange capacity) may overlook the role of the sludge itself in controlling the bioavailability of sludge-applied metals.

Several important processes are believed to operate in the sludge system to control solution metal activity. These include solid-phase equilibria, adsorption-desorption, chelation and oxidation-reduction. Attempts to characterize solid phase equilibria have assumed the presence of discrete metal forms such as CdS , Pb phosphates, etc.; however, Corey et al. (1981) and Corey (1981) have indicated that many of the trace metals may be coprecipitated with the major metal cations in sludge (Fe, Al, Ca) during the sewage treatment process. Predicting the solubilities of minor constituents of solid solutions are difficult. Studying the exchange reactions of metal cations on sludge is limited because of the present inability to accurately predict or measure free ion activities and because of the analytical problems associated with working at the very low solution concentrations found in sludge systems. Hendrickson and Corey (1981) have shown that, at low solution activities, trace metals are specifically adsorbed with respect to cations which have much higher solution activities, such as Ca or Mg. In addition, organically complexed dissolved metals interfere with the use of solid phase equilibria models.

Understanding the complexities of the sludge-metal system will require further basic research, but this understanding is critical to explaining the changes with time in metal bioavailability which occur when sludge-borne metals are added to soil. The role of the soil in this process will be discussed in a later section.

SLUDGE-BORNE METAL INTERACTIONS IN SOIL

REACTION PROCESSES IN SOIL

Most microelements (with the exception of boron) are strongly retained by soil and their concentrations in the soil solution are very low. In the Conference Proceedings, Lindsay (1973) pointed out that much of the work on soil-metal reactions has been empirical with very few basic studies to examine the precipitation reactions of metals in soils. Lindsay felt that, although the exact reaction products of Zn, Cd, Cu and Ni that precipitate in soils were not known, they likely involved substitution in crystalline minerals and amorphous precipitates as well as forming possible discrete silicate compounds; further, adsorption could control metal availability.

Ellis and Knezek (1972) reviewed the literature on metal adsorption by soils. They concluded that, in addition to cation exchange, metals are specifically adsorbed to functional groups on soil mineral surfaces. They did not feel that precipitation was an important control on ionic activity at the low metal ion activities normally found in soils, except at pH's above neutrality. Instead, adsorption dominated. Soil organic matter was considered a strong sink for some metals such as Cu and Zn, while the formation of soluble metal-organic complexes reduced free ion activities and metal adsorption by reactive soil surfaces.

Leeper in 1972 had also published an extensive review of metal reactions in soils and drew similar conclusions.

Page (1974), in his review which appeared the year after the Conference, examined the reaction processes of metals in soils, and came to the same conclusions as the authors previously cited. He did suggest, however, that, in the case of sludge-borne metals, the stability of metal solid phases in sludges may be as important as the chemical products formed between metals and soil constituents. He also pointed out that boron would not be retained by soil since it exists as undissociated boric acid at the pH's normally encountered.

Chaney and Giordano (1977) reported that the relative importance of the various metal-soil reactions in reducing plant-available metal levels was not clear, and that there was no research on the effects of several metals added simultaneously. The 1980 CAST Report indicated that "adsorption is the predominant mechanism of trace metal removal from dilute solutions by clay minerals, metal oxides, and organic matter, and by whole soils." The report also indicated that there is a strong pH-dependence of soil adsorption-desorption processes involving Cd and Zn, with pH affecting not only the metal species in solution but also the charge on the soil surface. The CAST (1980) Report also recognized that Cd and Zn could exist in soils as discrete precipitates, coprecipitates with iron or aluminum oxides or alkaline earth carbonates, and bound to soil organic matter.

Corey et al. (1981) suggest that adsorption on mineral surfaces is probably the dominant process controlling metal solution activities and can be described by a competitive Langmuir isotherm (Harter and Baker, 1977). They felt that metals are primarily specifically adsorbed because the selectivity of adsorption of metals

is on the order of 10^3 to 10^6 over ions like Ca^{2+} and Mg^{2+} . Because of the very low activities of metals in soil solution compared to the activities of more abundant cations (e.g. Ca, Mg, K), metals must be specifically adsorbed if they are to occupy a large percentage of the adsorption sites.

Corey et al. (1981) also concluded that, when metals are added with sludge, solution metal activities would be controlled by adsorption to soil mineral surfaces as long as the amount of metal added did not exceed the capacity of specific adsorption sites in the soil. In this region, metal activity should increase linearly with sludge metal addition. At high sludge application rates, metal binding sites on the sludge would control metal solubility, and further sludge additions would not increase metal activities. If this is true, the metal chemistry of a particular sludge which is applied to soil at high rates may be as important in controlling metal uptake by plants than the metal binding characteristics of the soil or the total amount of metal applied. This may be significant in our approach to regulating metal additions to soil, as discussed later. The considerations of Corey et al. (1981) also indicate that the ratio of metal to specific sorption capacity should be important in controlling metal ion activity.

METAL REVERSION IN SOILS

Chaney (1973) in the Conference Proceedings reported that "metals revert with time to chemical forms less available to plants." He gave the example of fertilizer Zn reversion which had been shown to be quite rapid. He indicated that the processes involved were poorly understood but were most rapid in calcareous soils.

In their 1977 review, Chaney and Giordano attributed the term "reversion" to Leeper (1972) and cited several cases of reversion of Cu, Zn, Fe and Mn when added to soil as fertilizer salts or chelates. Chaney and Giordano (1977) also reported that "in nearly every study on the effect of incubation on the extractability of microelements added as sludge or refuse compost, a continuing decline in extractability is observed."

The CAST (1980) Report carefully examined the data on residual availability of Cd and Zn to crops after termination of sludge application. The authors concluded that the residual effects were indeterminate. Although there was some evidence that bioavailability of the metals may remain constant or decrease over a period of years at a constant pH, they felt that soluble metal concentrations would increase if pH decreased.

It appears that, if metal reversion in soil does occur, the effects are small and/or slow, and can be reversed by increasing soil acidity. The lack of strong reversion processes in soil, especially for Cd (Lloyd et al., 1981), implies that land used for food-chain crops which has received large doses of sludge-borne metals must be managed for the foreseeable future so as to minimize metal uptake by crops. Further research is needed on the long-term changes of sludge-metal forms in the soil, and the effects of such factors as sludge-metal chemistry, soil chemical environment and sludge organic matter decomposition on metal availability to plants. The "time bomb" effect whereby sludge-applied metals become more available over time (at constant pH) suggested by Beckett and Davis (1979) has not been supported by research results.

EFFECTS OF SOIL PH, ORGANIC MATTER CONTENT AND CATION EXCHANGE CAPACITY ON SOIL METAL BINDING CAPACITY

Chaney (1973) in his Conference paper identified pH, cation exchange capacity (CEC) and organic matter (OM) content as soil factors controlling metal toxicity to plants. He considered that soil pH might be more important than the amount of metal added. Soil OM was viewed as a source of CEC for metal cations and also formed chelates with the metals, especially Cu and Ni. Chaney pointed out that, at low pH's, chelation would decrease metal availability to plants, but, at least in the case of Zn, chelation increased availability at high pH's. He stated that CEC was important in binding all cations, and "a soil with a high CEC is inherently safer for disposal of sludge and effluent than a soil with low CEC." The Conference Workshop Group 8 Plant Response-Toxic Chemicals felt that there was an immediate need for research on empirical correlations of the toxicity of metals with soil parameters, including CEC and pH.

Soil pH

Soil pH is the parameter most consistently identified in the literature as controlling metal availability. With the exception of Mo and Se, all of the microelements are more labile at low pH's. This is due to the hydrolysis of hydroxide species (Ellis and Knezek, 1972) and the solubility of other solid phase minerals such as carbonates and phosphate. Low pH also lowers the adsorption of metals to pH-dependent specific adsorption sites on mineral surfaces (H^+ is a competitive cation), and lowers the CEC of soil OM.

Sludge additions to neutral or slightly acid soil will tend to decrease pH somewhat depending on $CaCO_3$ equivalent content of the sludge (hardwater; lime in dewatering). Nitrification of sludge NH_3 , oxidation of organic matter and sulfur containing organic compounds in sludge, and oxidation of sulfides in anaerobic sludges all increase soil acidity, while the high buffer capacity of sludge organic matter tends to ameliorate these effects. On the other hand, sludge additions tend to decrease the pH of calcareous soils somewhat (CAST, 1980). At normal rates of sludge addition (no greater than the nitrogen requirement of maize), the soil buffer capacity and soil pH will determine the pH of the soil-sludge mixture. The CAST (1980) Report concluded that the ability of calcareous soils to maintain high soil pH with sludge additions greatly reduced the risk to the food-chain from Cd and Zn uptake by crops.

Chaney et al. (1978a) limed acid soils that had not received sludge for four years and found that Cd uptake was reduced. Liming also appears to reduce the availability of native soil metals (Sommers, 1980).

The soil pH level considered to be effective in reducing metal uptake by plants seems to be ~6.5. This value is widely reported (Chaney, 1973; CAST, 1976; CAST, 1980) and is required by USEPA (EPA, 1979a) for sludge applied to land for the production of food-chain crops. This pH level is usually attributed to Chumbley (1971) who developed guidelines in England for the control of phytotoxic levels of Zn, Cu and Ni in soils.

There is no indication from the work of Chumbley and others that there is any basis for selecting this pH other than observed metal uptake (CAST, 1980).

Solid-phase equilibria of the metals in soil may provide evidence for the effect of pH on metal solubility (Lindsay, 1979) but that analysis has not been done, and is complicated by not knowing if the solid phases controlling metal solubility are sludge derived or are soil minerals. Also, activities of organometallic complexes are not as affected by pH as are free ion activities. There is no evidence from recent research that pH 6.5 is not an effective control for metal uptake by crops, and, except for acid soils strongly buffered by Al, this pH level is easily attained and maintained by periodic liming. On more acid soils, as found in unglaciated regions of the eastern U.S., raising pH to near 6.5 is difficult and expensive. Once attained, this pH can be maintained with lime additions every two to three years.

Cation Exchange Capacity (CEC)

With the exception of As, Se, Mo and B, the elements of concern are all cations and, as such, are attracted by electrostatic forces to the predominant negative charges on soil minerals and organic matter. Ellis and Knezek (1972) pointed out that the metal cations, in addition to cation exchange, are specifically adsorbed by covalent bonds to functional groups on clay surfaces. They also reviewed early work (Bower and Truog, 1941; DeMumbrum and Jackson, 1957; Hodgson, 1963) which showed that hydrolysis of aquo groups coordinated to the metals significantly affect their adsorption by soils.

Most authors (Chaney, 1973; Haghiri, 1974; Latterell et al., 1976; CAST, 1976 and 1980) recognize CEC as one of the soil properties which are related to soil retention of metals. Leeper (1972) was the first to suggest that soil CEC be used as an index of the amount of metal (Cu, Ni, Zn) which could be safely added to soil without causing phytotoxicity. The North Central Regional Research Committee on Land Application of Sewage Sludges (NC-118) (EPA, 1980) proposed in 1974 that medium textured soils in the region could safely accept cumulative amounts of Cd, Ni, Cu, Zn, and Pb based on their relative phytotoxicities (in the case of Ni, Cu, Zn) and risk of food chain contamination (Cd, Pb) as well as their relative uptake by crops. The Committee in 1976 expanded the guidelines on cumulative metal additions to distinguish between fine, medium and coarse textured soils. Soils were arbitrarily divided into three groups by CEC (< 5 , $5-15$, > 15 meq/100g soil) with cumulative additions as given in Table 2. (The Ni levels were later raised to be the same as for Cu).

In the case of several of the metals, particularly Cd, there was no research evidence to show that there was a direct link between Cd uptake by plants and CEC. The Committee felt, however, that CEC was a readily and routinely measured soil property that was directly related to the ability of a soil to minimize Cd solubility. The Committee also recognized that the effects of CEC are compounded by the specific sorption characteristics of soil organic matter, Fe, Mn and Al oxides. OM binds metals by chelation as well as by cation attraction. Fe, Mn, and Al oxides can specifically adsorb metals yet do not have sufficient net negative charge to bind metals by cation exchange. Increasing pH will increase CEC of organic matter and other soil minerals with pH-dependent charge, but an increase in metal retention may also be due to decreased solubility of the metals adsorbed to solid phase minerals.

The 1980 CAST Report reviewed the literature on effects of CEC on Cd and Zn uptake by crops and concluded that it was difficult to establish a direct

TABLE 2. CUMULATIVE METAL ADDITIONS IN SOIL

	Cumulative Metal Additions (lbs/acre)		
	<5 meq/100g	5-15 meq/100g	>15 meq/100g
Cd	5	10	20
Ni	50	100	200
Cu	125	250	500
Zn	250	500	1000
Pb	500	1000	2000

relationship between CEC and uptake because most of the experiments were confounded by organic matter or pH effects. The Report stated that "...CEC is best viewed as a general, but imperfect, indicator of the soil components that limit the solubility of Cd and Zn (i.e., organic matter, clays, and hydrous oxides of iron, aluminum and manganese) instead of a specific factor in the availability of these metals."

Corey et al. (1981) determined relative selectivity coefficients of Cd with Zn, Cu, Ni and Fe for EDTA, and solid phase and soluble complexes in a soil which had received 320 mt/ha of sludge. Selectivity coefficients were similar for the three types of metal complexes and, even at the relatively high metal levels in the soil, there was still considerable selectivity for the different metals. This indicates that these specific sorption sites are much different than the cation exchange sites suggested by Bittell and Miller (1974) and Cavallaro and McBride (1978). Corey et al. (1981), however, do not distinguish between sludge and soil sites in their system.

Further research is needed to clarify the role of specific versus non-specific metal absorption, and to determine the nature, persistence and relative importance of sludge versus soil metal-binding sites.

Soil Organic Matter (OM)

Soil organic matter can bind metals through cation exchange and through the formation of organometallic complexes (Mortensen, 1963; Hodgson, 1963; Schnitzer, 1969). On the other hand, soluble metal-organic complexes can reduce the absorption of metals and increase their availability (Stevenson and Ardakani, 1972). Soluble chelates and complexes allow faster diffusion from soil solid phases to plant roots (Lindsay, 1974). Stevenson and Ardakani (1972) reviewed the relative stabilities of metal-organic complexes of the trace nutrients and found at pH 5 that they were in the order: Cu > Pb > Fe > Ni > Mn > Co > Zn. More recent work (Mahler et al., 1980) has shown that only a small percentage of Cd added with sludge to soil is organically complexed.

It has only been in the last six or seven years that researchers have begun to characterize the role of sludge and soil organic matter in metal complexation and retention. Sposito and co-workers (Holtzclaw et al., 1976, 1978) extracted the humic and fulvic acid fractions of sewage sludges and found that metals differ in their distribution in these fractions. Other workers (Davis and Leckie, 1978; Newton et al., 1976; Elliott and Huang, 1979; Chubin and Street, 1981; Elliott and Denny, 1982) have studied the effects of organic complexing ligands on the adsorption of metals by soils and minerals. Ligands such as EDTA which form strong metal complexes reduced metal adsorption while other organic ligands had less effect. Adsorption of the ligand itself can also affect metal adsorption.

While it is clear that both sludge and soil derived organic matter can affect metal retention in soil and, therefore, metal uptake by plants, this area remains poorly understood. Microbial biomass may also bind metals (Kurek et al., 1982). Because of its highly complex nature, advances in the knowledge of metal-organic matter reactions have been slow. However, recent developments in analytical methodologies should provide greatly needed new information on the chemistry of

organometallic complexes and their role in the retention and bioavailability of metals in soil.

EXTRACTION PROCEDURES FOR MEASURING BIOAVAILABILITY OF SLUDGE BORNE METALS

Melsted (1973) in his Conference paper stated that "from past experience, and the inability to establish uniform soil testing methods for the determination of available essential heavy metals like zinc and copper under a wide range of soil conditions, the likelihood of developing standard methods of analyses for the toxic elements are rather remote." Melsted suggested that, although methods of soil analysis for available forms of some methods had been developed on a regional basis, procedures for other metals can only be developed when their available chemical forms are known. Workshop Group No. 8 identified an immediate need to develop laboratory diagnostic techniques for measurements of available toxic metals in soils.

Cox and Kamprath (1972) in their review of micronutrient soil test procedures discussed tests that were based on four types of nutrient pools: (1) water soluble, (2) exchangeable, (3) adsorbed, chelated or complexed and (4) minerals. Soluble concentrations of the micronutrient metals (and other metals) are very low in soils, and water extraction has been of little value as an extractant for metals. However, hot water-extractable B has long been used as an index of boron availability to crops (Wear, 1965). Exchangeable Zn and Mn have been successfully correlated with plant uptake (Cox and Kamprath, 1972), but the exchangeable levels of most metals in soil are low. Cox and Kamprath (1972) felt that metal release from soil minerals would contribute very little to plant uptake from highly weathered soils, but could be an important source in arid and semi-arid environments. They did not propose methods for extraction of this pool.

Although Cox and Kamprath (1972) discuss some early work on the development of micronutrient soil tests using complexing agents such as EDTA, most of the development of these tests and general use of these procedures have followed since that time. The most routinely used soil test procedure for available metals is DTPA-TEA extraction (Lindsay and Norvell, 1978) which is primarily used for Zn, Cu, Fe and Mn. In recent years it has also been used to extract other metals (Bingham et al., 1975; Kelling et al., 1977, Street et al., 1977). Korcak and Fanning (1978) compared DTPA extraction with extraction with double acid (0.05N HCl + 0.025N H₂SO₄) for Cd, Cu, Ni and Zn applied to soil as inorganic salts or in sewage sludge. The soil was at pH 5.6 and 6.5. The two procedures were highly correlated with each other, but the DTPA procedure was more sensitive to reduced solubilities of Zn and Cu at the higher pH. Neither procedure correlated well with plant uptake when the metal was applied with sludge, although correlations were improved when the data for the two pH regimes were separated. The DTPA-TEA method is being replaced by an ammonium bicarbonate-DTPA test which allows multielement analysis by plasma spectrometry (Soltanpour and Schwab, 1977).

Baker and his coworkers at Pennsylvania State University (Baker and Amacher, 1981; Baker, 1980; Baker et al., 1976) have developed a quantity/intensity method of soil testing for nutrients and trace metals. They use DTPA as a means of equilibrating with soil metal and make interpretations based on both the labile pool of metal able to equilibrate with DTPA (quantity) as well as

the free ion activity (intensity). Baker and Amacher (1981) give high, normal and low quantity and intensity levels for Al, Pb, Ni and Cd.

Haq et al. (1980) examined the ability of nine extractants to predict metal uptake by swiss chard from 46 Ontario soils with varying degrees of metal contamination. No one extractant successfully predicted uptake of Cd, Ni, Cu or Zn, but several of them, including DTPA and ammonium acetate gave satisfactory results when combined in the regression equation with other soil properties such as pH, % OM, CEC, etc.

More recently, workers have attempted to characterize Cd in soil solution by saturation extraction or extraction with 0.1M $\text{Ca}(\text{NO}_3)_2$ (Corey et al., 1981; Lampert et al., 1982). Mahler et al. (1982) found that saturation extract Cd was correlated with Cd concentration in lettuce, chard, tomato and corn, but the relationships were different for calcareous and acid soils. There was more extractable Cd in the calcareous soils than the acid soils, but this was not reflected in plant uptake. This may have resulted from use of Cd SO_4 -amended sludge, as other studies did not find this pH effect on Cd solubility. Corey et al. (1981) suggest that saturation extracts or electrolyte extraction may be more sensitive to changes in the soil-sludge chemical environment than more rigorous extractions, but the results of Mahler et al. (1982) indicate that there are factors other than solution concentration affecting the uptake of metals by plants.

As identified at the 1973 Conference, there is a need to develop reliable soil test procedures for the determination of available metals in soil. However, to date no such test or tests are available, and it is likely that no one test or tests will be applicable to all metals on all soils. If this is true, then further research should emphasize regional development of soil test procedures for specific metals and crops.

MOVEMENT OF SLUDGE BORNE METALS BY RUNOFF AND LEACHING

Workshop Group 8 identified as a long term research needs a trace element inventory which would include "leakage from the soil-root zone" and "erosion from surface soils into lakes and streams." Only a very small fraction of trace metals in soils is soluble. Page (1974) indicates that the published literature show that the concentrations of the metal cations in neutral soil are usually $<0.05 \mu\text{g/mL}$. In the range of pH's common to soils (5-8.5) Page reported that soluble metal concentrations do not exceed $0.25 \mu\text{g/mL}$. Because of this, metal cations do not leach readily from soil. However, under conditions of heavy applications of sludge and low soil pH's, there have been reports of metal movement to depths up to several meters. Lund et al. (1976) found increased levels of Cr, Cu and Zn to a depth of 2m beneath a sludge drying bed that had been used for more than 20 years, while elevated Ni and Cd concentrations were detected at 3.5m. Kirkham (1975) found movement of Cd, Cu, Ni and Zn to a depth of 61cm below a 3-year old sludge lagoon. Hinesly et al. (1972) and Boswell (1975) found movement of metals to depths up to 45 cm with heavy applications of sludge (135-168 mt/ha) to agricultural land. Emmerich et al. (1982) studied the movement of sludge-applied metals to soils in a column study. They found that no movement of metals had occurred from the 476 mt/ha sludge application after leaching with 5m of water over a 25-month period. Although soil pH's were in the range 5.2-8.0 prior to

sludge application, nitrification of sludge nitrogen greatly lowered pH in the soil zone below the sludge.

At annual sludge application rates < 15 mt/ha which are recommended for efficient crop removal of sludge-nitrogen, leaching of metals should pose little threat to groundwater resources for all but those sludges with very high metal levels.

Because of the high retention of metals by soils, loss of metals by erosion and runoff transport of sediments should pose a greater threat to water supplies than leaching. This would be particularly true in instances of heavy applications of sludge to land adjacent to water bodies. However, there are no research reports that indicate that this occurs (Dowdy et al., 1980). Even if some erosion and transport of soil containing sludge-applied metals occurs, the low solubility of the metals will result in very low metal levels in the stream or lake water. Proper site selection and sludge application management should be adequate to protect our water resources from metal contamination from surface runoff and erosion.

METAL UPTAKE BY PLANTS

INTRODUCTION

Uptake of sludge-borne metals by plants is important for three basic reasons. First, plants require several micronutrient elements for normal growth; sludge can serve as a Zn, Cu, or Fe fertilizer. Second, if excessive amounts of some elements are absorbed by plants, reduced yield or plant death can result. This process is called phytotoxicity, and sludge Zn, Cu, and Ni have caused phytotoxicity when poorly managed. Third, plant uptake of some microelements is the primary route for them to cause food-chain risk.

In 1973, little was known about plant uptake or phytotoxicity of sludge-borne metals (Chaney, 1973). Results from excessive application of microelement fertilizers or pesticides, or on soils developed over metal-rich geologic anomalies provided nearly all the field data. Poor sludge practices in the United Kingdom provided evidence that sludge metals could cause phytotoxicity (Chaney and Giordano, 1977).

Very much has been learned about metal uptake by plants in the last decade. However, our knowledge remains incomplete -- especially on phytotoxicity, and on basic chemistry of metals in sludge-amended soils. Many of the examples reviewed in this section will deal with Cd, partly because of the special interest in Cd, and partly because this interest resulted in much research on Cd.

SLUDGES AS MICROELEMENT FERTILIZERS

Chaney and Giordano (1977) summarized results from studies of using sludge to correct micronutrient deficiencies, and noted that "It seems reasonable that wastes which are otherwise safe for use on cropland could be applied to satisfy N or P requirements, and the waste could simultaneously correct any Zn, Cu, etc., deficiencies." Since that time, McClaslin and O'Connor (1982) have shown that sludge could also correct Fe deficiency of sorghum in New Mexico soils. Irradiated raw sludges were more effective than digested sludge, perhaps indicating that

reduction of soil iron in inert crystalline ferric oxides to form the more plant available hydrous ferric oxide contributes to Fe availability along with sludge organic matter-bound and chelated Fe.

At this time, sludge has been experimentally shown to correct Zn, Cu, and Fe deficiencies. Boron, Mn, and Mo in sludge are seldom at high enough concentrations to serve as fertilizers in the field. Composted sludge provided all required microelements for horticultural potting media (Chaney et al., 1980).

PHYTOTOXICITY

Excessive heavy metal absorption can kill a plant, or allow normal environmental stresses to kill the plant. Of the elements commonly present in municipal sludge, Zn, Cu, Ni, and Mn are likely to cause phytotoxicity with improper management of soil pH or cumulative metal application. In a few industrially polluted sludges, Co could also cause phytotoxicity. Sludge Mn is not generally a cause of toxicity, but soil Mn can become more available due to sludge use, and Zn plus Mn phytotoxicity can occur in strongly acidic soils (White et al., 1979b).

Excessive Cu, Ni, or Co usually cause injury of plant roots, and inhibit translocation of Fe from roots to shoots; then phytotoxicity is expressed as yellow (chlorotic) young leaves which is metal-induced Fe-deficiency. Zinc and Mn are translocated more freely to the leaves; although Zn and Mn can injure roots and induce Fe-chlorosis in some species, their toxicity is usually manifested through injury of older leaves and reduction of plant growth through interference with biological processes (Foy et al., 1978). Some refuse composts are rich enough in B to injure sensitive crops when applied at high rates (Purves and Mackenzie, 1974; Sanderson, 1980).

Potential phytotoxicity is affected strongly by soil pH, other soil properties, crop species and cultivar, sludge metal concentration, and climatic factors. As shown in Table 3, soil pH, sludge application rate, and crop strongly affect phytotoxicity. Most vegetable crops and legumes (dicots) are relatively sensitive to excessive sludge metals in acidic soils.

Although soil organic matter or CEC are important in toxicity of added metal salts (see White and Chaney, 1980), there is little evidence of the importance of these properties for sludge-applied metals (CAST, 1980). Sludge metal sorption properties can quickly dominate over soil properties in controlling metal uptake (Corey et al., 1981). This could result from sludge organic matter, hydrous Fe oxide, and/or phosphate. Webber et al. (1981b) found that sludge Cu could not cause phytotoxicity unless the sludge contained appreciably over 1000 µg/g Cu. High metal concentrations are also implicated in the studies by Williams (1980) and Marks et al. (1980) where sludges rich in Zn, Cu, or Ni caused severe yield reductions in vegetable crops when soil pH was low.

Most commonly, sludge metal phytotoxicity is observed only with low soil pH (Marks et al., 1980; Chaney et al., 1978a). Lutrick et al. (1982) applied a low-metal liquid digested sludge to an acidic fine-textured soil in Florida. At high cumulative sludge rates (300 Mt/ha; over 700 kg Zn/ha), soil pH declined substantially due to oxidation of sludge N and S, reaching pH 4.6. Soybean suffered

TABLE 3. RELATIVE SENSITIVITY OF CROPS TO SLUDGE-APPLIED HEAVY METALS (Chaney and Hundemann, unpublished)*

Very Sensitive†	Sensitive‡	Tolerant§	Very Tolerant#
chard lettuce redbeet carrot turnip peanut ladino clover alsike clover crownvetch 'Arc' alfalfa white sweetclover yellow sweetclover weeping lovegrass Lehman lovegrass deertongue	mustard kale spinach broccoli radish tomato marigold zigzag, Red, Kura and crimson clover alfalfa Korean lespedeza sericca lespedeza blue lupin birdsfoot trefoil hairy vetch soybean snapbean Timothy colonial bentgrass perennial ryegrass creeping bentgrass	cauliflower cucumber zucchini squash flatpea oat orchardgrass Japanese brome grass switchgrass red top buffelgrass tall fescue red fescue Kentucky bluegrass	corn sudangrass smooth brome grass 'Merlin' red fescue

* Sassafras sandy loam amended with a highly stabilized and leached digested sludge containing 5300 mg Zn, 2400 mg Cu, 320 mg Ni, 390 mg Mn, and 23 mg Cd/kg dry sludge. At 5% sludge, maximum cumulative recommended applications of Zn and Cu are made.

† Injured at 10% of a high metal sludge at pH 6.5 and at pH 5.5.

‡ Injured at 10% of a high metal sludge at pH 5.5, but not at pH 6.5.

§ Injured at 25% high metal sludge at pH 5.5, but not at pH 6.5, and not at 5% sludge at pH 5.5 or 6.5.

Not injured even at 25% sludge pH 5.5

Zn + Mn phytotoxicity; seedling leaves contained as high as 1190 µg/g Zn and 725 µg/g Mn. Toxicity was easily corrected by liming. In a field study with a low metal sludge studied at soil pH 6.2 and 5.4, the soil received 298 kg Zn/ha at 224 Mt/ha of applied sludge. Romaine lettuce contained only 67 and 225 µg/g Zn at the respective pH levels (Chaney et al., 1932).

Crops differ remarkably in metal uptake, and in tolerance of soil metals (Table 3). Crops differ somewhat in tolerance of foliar Zn, Ni, and Cu, and substantially in tolerance of foliar Cd (Bingham, 1979). Mahler et al. (1978) and Baxter et al. (1974) noted that Zn or Cd in leaves associated with 25% yield reduction of lettuce (Cd) or chard (Cd, Zn) varied with soil pH; higher foliar metal levels were tolerated in acid soils.

Further, crops differ in relative toxicity of soil Zn, Cu, and Ni, and soil pH affects the relative toxicity coefficients for added soil metals (Mitchell et al., 1978). Beckett and coworkers have studied relative toxicity and additivity of metal toxicity (Beckett and Davis, 1978; Beckett and Davis, 1979), although they focused only on foliar metal levels. Most of their conclusions are based on nutrient solution or sand culture studies using soluble metal salts, which may underestimate tolerance of foliar metals. They concluded that Zn and Cu are largely antagonistic rather than additive. Metal additivity did not occur until 0.5 to 0.67 of the "upper critical" foliar concentration was reached. They concluded that the Zn (equivalent) equation of Chumbley (1971) seriously underestimated safe sludge loadings because it presumed total additivity. Mitchell et al. (1978) came to a similar conclusion because the equation's relative toxicity coefficients for Zn, Cu and Ni (1:2:8) were higher than observed in a metal interaction/additivity study with wheat and lettuce. They also reported that excessive metals could interact by competing for sorption sites in the soil. Added Cu or Zn increased Ni in soil solution and Ni uptake by crops and hence Ni phytotoxicity.

Knowledge of tolerance of foliar metal concentrations has progressed, although agreement among researchers is incomplete. Table 4 summarizes foliar metal levels associated with appreciable yield reduction by several authors. Part of these differences may come from differences in utilization of chelated Fe in nutrient solution by monocots and dicots. Davis and Beckett (1978) found barley tolerated only 200 µg/g foliar Zn in sand culture (upper critical level), while Boawn and Rasmussen (1971) found small grains tolerated 500 µg/g foliar Zn when grown in soil (25% yield reduction). White et al. (1979a) found tolerance to 400-600 µg/g foliar Zn among soybean cultivars.

COMMON ERRORS IN STUDY OF TOXIC ELEMENT UPTAKE BY PLANTS

During the last decade our understanding of appropriate experimental procedures for study of sludge-applied metals has greatly improved. Researchers have noted several major errors in experimental methods (CAST, 1980). First, the source of metals added may strongly affect the result, and second, the location in which the experiment is conducted may affect the results. Potential problems in nutrient solution vs soil studies were noted above.

The first error is usually called the "salt vs sludge" error. When metals are added as soluble metal salts (sulfate, chloride, nitrate), they nearly always cause greater plant uptake and toxicity than when applied in sludge. Metals in digested

TABLE 4. DIFFERENT ESTIMATES OF FOLIAR METAL CONCENTRATIONS ASSOCIATED WITH APPRECIABLE YIELD REDUCTION DUE TO SINGLE ELEMENT METAL TOXICITY

Element		Melsted (1973)	Chaney et al. (1978a)	Davis et al. (1978) Davis & Beckett (1978) Beckett & Davis, (1977)	
				25% YR*	10% YR
		mg/kg dry leaves			
19	Zn	300	500	200	290
	Cu	15	20-40	20	20
	Ni	3	50-100	11	26
	Cd	3	varies	8	15
	Mn	300	500	--	--

* Denotes yield reduction

sludges should be much nearer to equilibrium with sludge organic matter, with sparingly soluble inorganic compounds, or occluded in CaCO_3 or other minerals (Corey et al., 1981). Bloomfield and McGrath (1982) recently reported that a significant error remains even when metals are incubated with sludge after digestion. Davis and Carlton-Smith (1981) reported results from adding metals to raw sewage to subsequently obtain digested sludges with desired compositions. Uptake of Cd and Zn by radish was similar for the prepared sludges and sludges obtained from sewage treatment plants.

Sludge supplies both organic matter and hydrous Fe and Mn oxides, both of which increase the specific metal sorption capacity of the soil (Soon, 1981; Garcia-Miragaya and Page, 1978) and reduce plant availability of Cd (Singh, 1981). Further, metal salts lower the pH of the soil by displacing adsorbed H^+ ; few authors have corrected soil pH to the level of the control. Alternatively, soluble metal acetates raise the soil pH as the acetate is oxidized, as do metal oxides or carbonates. Adding equimolar mixtures of NiSO_4 and $\text{Ni}(\text{Acetate})_2$ caused little change in soil pH even at very high Ni applications which lowered pH over 1.5 units when applied as NiSO_4 (Chaney and Leech, unpublished). Many authors have reported the salt-sludge difference (e.g. Dijkshoorn et al., 1981). In light of research summarized in this paper, it is inappropriate to purport that metal salt additions simulate sludge metal additions.

The second error is generally called the "greenhouse vs field" error. Greenhouse and growth chamber studies offer greater manageability and reproducibility and lower cost than field studies (and do not suffer from foraging wildlife). However, crop Zn, Cd, and Mn are increased 1.5 to 5 fold over field studies with the same soil, sludge, and crop (deVries and Tiller, 1978; deVries, 1980). Davis (1981a) also found higher uptake of Cu in pots (and in greenhouse > outside) than in field. This appears to result from 1) use of $\text{NH}_4\text{-N}$ fertilizers which lowers soil pH more in pots than in the field; 2) higher soluble salt levels in pots than field due to smaller soil volume for required fertilizer salts; 3) confinement of plant roots to the small volume of treated soil in pots, and 4) abnormal watering pattern and relative humidity in greenhouse pot studies. The smaller the pot, the greater the error. Another common error in pot studies is inadequate supply of fertilizer nutrients to obtain maximum growth rates (Terman, 1974).

The pH of the soil immediately adjacent to plant roots (the rhizocylinder) is especially important in plant uptake of microelements. When roots absorb $\text{NH}_4\text{-N}$, the pH of the rhizocylinder soil declines, and when the roots absorb $\text{NO}_3\text{-N}$, the pH rises. Thus, the form of N absorbed by the root has a strong influence on metal cation uptake (Barber, 1974). In the field, most crop N is absorbed from the soil as $\text{NO}_3\text{-N}$; this would raise rhizocylinder pH (Nye, 1981). Use of $\text{NH}_4\text{-N}$ fertilizers also causes the pH of the bulk soil to decline since H^+ is generated when $\text{NH}_4\text{-N}$ is oxidized to $\text{NO}_3\text{-N}$ (see Jolley and Pierre, 1977).

When sludges supply metals, the uptake depends on period since application. Rapid breakdown of organic matter (especially at higher sludge rates) supplies organic ligands and $\text{NH}_4\text{-N}$, both of which facilitate metal diffusion and uptake (see Barber, 1974; Lindsay, 1974; Wallace et al., 1977). Radish absorbed very high levels of Cu and Zn and suffered phytotoxicity when grown on freshly amended heated (37°C) soils (Sheaffer et al., 1981); five crop years later, soil temperature

had almost no effect on uptake, and healthy crops resulted (Chaney et al., unpublished) (Table 5). The higher soluble salts in pot studies or high rates of recent sludge additions can increase soluble metals by forming complexes (Cl) or ion pairs (SO₄) with metals, thereby increasing metal diffusion and uptake (Bingham, 1980).

Thus, although pot studies in greenhouse and growth chamber allow the control of experimental variables needed to characterize details of the soil-plant interactions of metals, most researchers agree that regulations must be based upon field research. First year results, and annual sludge rate in excess of crop N requirements cause errors even in the field. Further, the error due to study of high metal concentration sludges discussed earlier precludes obtaining results applicable to use of low metal sludges in agriculture.

PLANT DIFFERENCES IN METAL UPTAKE AND TRANSLOCATION

Plant Factors

Crop plants differ widely in uptake of an element, all other factors held constant (Chaney and Giordano, 1977; Sommers, 1980; Peterson and Alloway, 1979). Growing on the same sludge-amended soil, spinach may contain 10 times more Zn than tall fescue, orchardgrass 15 times more Ni than corn, and chard 5 times more Cu than tall fescue. A recent report by Davis and Carlton-Smith (1980) shows relative concentration of Zn, Cu, Ni, Cd, Pb in foliage and edible parts of 28 species grown in 10 kg pots of soil from two long term sludge farms. This report is the widest published comparison of metal uptake by crops from metal rich soils.

Some plant differences are inherent in the uptake by roots (can be observed in nutrient solutions). Other differences in metal uptake are due to soil-plant interactions, and can be observed only in soil studies. And still other plant differences can result from differences in root distribution in the soil with depth, and can only be found in field studies.

To date, plant differences are discovered by empirical research. Although specialists can select appropriate crops for specific metal-rich soils, (above levels shown in Table 1), they have a very limited data base to work from. Climate and soil drainage must also be considered in selecting crops for a particular soil.

Factors Affecting Microelement Translocation

After a microelement enters the root cells, its translocation to shoots is controlled by metal and plant characteristics. Root cell sap contains high levels of organic acids and amino acids which can chelate many elements. Membrane surfaces and proteins contain functional groups which can chelate some metals. Thus, a metal can be caught in the roots if chelates formed in the root cells sap can not be transported into the xylem. ~~Xylem is the system of non-living tubes in plants in which water and nutrients are translocated from roots to shoots.~~ Most metals reaching the xylem are pumped into it by specialized cells. These cells, and chelates formed in the root cytoplasm, control whether a plant translocates a metal. Jarvis et al. (1976) noted wide variation among species in percent of absorbed Cd which was translocated to shoots; species ranged from 10-to-90%

translocated. Crops often called Cd "accumulators" translocated a high percentage of absorbed Cd.

Generally, Zn, Cd, Mn, B, Se, and Mo are easily translocated because they are weakly chelated. Copper, Ni, and Co are more strongly chelated; a much smaller portion of the absorbed Cu is translocated to shoots than of Zn. Pb, Cr, and Hg are so strongly held in the root cells that very little is translocated to the shoots of crop plants. Research has characterized chelation of Fe, Ni, Cu, Co, Zn, and Cd in xylem sap, but only Fe citrate has been unequivocally identified (Tiffin, 1977; Foy et al., 1978; White et al., 1981; Cataldo et al., 1981). Amino acids control translocation of Ni and Cu in crop plants (Tiffin, 1977; Cataldo et al., 1978). Citrate probably chelates Zn and Cd in xylem sap (White et al., 1981; Chino and Baba, 1981), although Cataldo et al., (1981) concluded that plant-absorbed Cd appeared in non-citrate complexes.

Transport to Storage Organs

Many crops form storage or reproductive organs (edible roots or tubers; fruits; seed) which are used as food or feed rather than the whole plant shoot. Crops differ widely in botanical type of storage organ formed, and in translocation of microelements into the organ as it forms. The stored fat, protein, and starch come from sugars and amino acids via phloem from foliar photosynthesis. Some species have close control on composition of their storage organs (maize; beans; potatoes; fruits), while storage organs of other crops are readily increased in microelements when the leaves are increased (wheat, oat, rice, soybeans; root crops) (CAST, 1980). Interactions among metals may occur not only during root uptake, and translocation to shoots, but also during transport to edible tissues (Chaney et al., 1976). (2) Although vegetable crop transplants grown in media containing sludge compost may have increased Cd levels, edible portions of mature crops were not increased in Cd (Sterret et al., 1982).

(83) A further source of difference among crops can be expressed as a result of food processing. When many grains are processed into "refined" flour products, the starchy endosperm is separated from the mineral and fiber rich bran. Metals in rice, wheat, and corn refined products are substantially lower than in whole grain products, although there is increasing consumption of whole grain feeds over more refined products (Hinesly et al., 1979b; Chino, 1981; Kitagishi and Obata, 1981). However, oat groats contain the bulk of metals in oat grain (Kirkleis et al., 1981), and soybean cotyledons and normal soy protein products are as high in Cd as the whole grain (Braude et al., 1980). (27)

CULTIVAR DIFFERENCES IN METAL UPTAKE.

The potential for breeding crop cultivars with reduced metal concentrations or greater metal tolerance was noted in the 1973 Work Group 8 report. Some very promising results were reported by Hinesly et al. (1978, 1980) for differences in Cd and Zn uptake among maize inbreds and maize hybrids. Bache et al. (1981) found smaller differences in Cd in foliage or grain of maize cultivars adapted to New York. These results indicate that Cd-excluder cultivars are available for use on dedicated sludge farms. Some of the early misunderstandings about crop uptake of Cd resulted from these appreciable differences in Cd uptake among maize cultivars used by several researchers (CAST, 1980).

(1,2) Soybeans, however, differ much less than corn in relative Cd and Zn uptake and tolerance (Boggess et al., 1978; White et al., 1979a). Although lettuce cultivars differ in Cd and Pb uptake, the range is small (CAST, 1980). Whether these smaller differences result from the smaller genetic base of adapted soybean and lettuce cultivars, or other differences between these crops is unknown.

(1,1) Harris et al. (1981) recently reported on studies of differences in metal uptake among six potato cultivars (3 early, 3 main crop) when they were grown on an old sludge farm. The soil contained 1811 $\mu\text{g/g}$ Zn, 19.6 $\mu\text{g/g}$ Cd, 752 $\mu\text{g/g}$ Cu, and was pH 6.6; these metal concentrations exceed median levels in sludges. Yet the washed, unpeeled potato tubers contained only normal Cd levels (mean = 0.28 $\mu\text{g/g}$ dry), and did not differ significantly among cultivars.

Wheat cultivars also differ in Cd transport to grain. On soils containing background levels of Cd, a substantial difference was found among types of wheat (Meyer et al., 1982). Durum types were much higher in grain Cd (140 $\mu\text{g/kg}$) than soft red spring, soft red winter, hard red spring, or white wheats (44 $\mu\text{g/kg}$). Durum wheats are a different species (tetraploid) than other wheats (hexaploid). Grain Cd was not significantly correlated with soil Cd, although low soil pH allowed slightly higher grain Cd for the non-durum samples. (102)

Andersson and Pettersson (1981) reported on variation in grain Cd among wheat cultivars grown in Sweden. A small range was observed. Hinesly (T. D. Hinesly, Dept. Agronomy, Univ. Illinois, personal communication) examined Cd in grain of nine soft red winter wheat cultivars grown on pH 5.5 sludge-amended strip mine soils (34 $\mu\text{g/g}$ Cd). Cultivars did not vary significantly in grain Cd at average 3.0 $\mu\text{g/g}$ levels (2.4-to 3.4 $\mu\text{g/g}$). (24)

ROLE OF SLUDGE-BORNE METAL SORPTION CAPACITY,

→ A number of alternative explanations have been suggested during the last decade for the apparently different effects of sludge-applied Cd on crop uptake of Cd. These include: 1) that repeated additions are different than single additions, also stated as annual additions of sludge Cd cause different Cd uptake than cumulative additions; 2) that sludge-borne Cd has either some or no persistent effect on crop Cd; and 3) that Cd salts, high Cd sludges and low Cd sludges have unequal effects on crop Cd. These are important differences since they would affect the regulatory strategy needed to protect humans from excessive dietary Cd (Ryan et al., 1980). Recent re-analyses of the data on which these different explanations are based have led to an underlying mechanism or model which relates these difficult questions. (105)

At the 1980 meeting of the W-124 Regional Research Committee, Corey introduced the concept that sludge is richer than soils not only in Cd, but also in Cd-specific sorption sites. These specific sorption sites sorb Cd on the order of 10^6 times more strongly than they bind Ca (Corey et al., 1981). He reasoned that, as sludge application rate increases, Cd activity will initially increase in the sludge-soil mixtures. The increase should be nearly linear at low sludge rates, as the soil Cd-specific sorption sites become progressively saturated. At still higher sludge rates, the soil Cd-sorption sites become saturated, and equilibrium Cd activity is now controlled by the ratio of Cd in sludge to Cd-sorption sites in the sludge. Further increase in sludge Cd application would produce little or no further

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increase in Cd activity. Soil pH would affect Cd activity regardless of the source of the Cd-sorption sites. These concepts are discussed in Corey et al. (1981) and are strongly supported by field results with sewage sludge on several Wisconsin soils (Fujii, 1988) (106), (35)

The implications of this model include 1) Cd is adsorbed (hence labile), rather than precipitated as an inorganic compound in soils; 2) Cd activity in soil-sludge mixtures will be affected by sludge Cd concentration; 3) the concentration of Cd in crops may be a linear function of sludge-applied Cd only at low sludge additions, and 4) relative crop availability of an increment in soil Cd will depend on the history of sludge application for the soil. The CAST (1980) report concluded that these were indeed the characteristics of sludge amended soils. (3)

Street, et al. (1977) found that activity of Cd in soils was below that controlled by the least soluble inorganic Cd compounds for nearly all soils. Thus, they concluded that sorption controlled Cd activity. Further, Lloyd et al. (1981) reported that the Cd in soils of long-term sludge farms was nearly 100% labile.

Sludge applied Cd, as well as other Cd sources, remain available for plant uptake for many years in acidic soils, i.e., Cd is persistent. Studies of crops grown on long-term sludge farms indicate crops can absorb increased Cd concentrations for at least as long as 20 years after the last sludge application (Chaney and Hornick, in CAST, 1980; Mahler and Ryan, 1982; Kirkham, 1975; Chaney et al., 1977; LaConde et al., 1979; Richardson, 1980; Chumbley and Unwin, 1982; Davis and Carlton-Smith, 1980). Cd is also persistent from phosphate fertilizers (Williams and David, 1973), from mine waste contaminated soils (Davies and Ginnever, 1979; Takijima and Katsumi, 1973), and in very old naturally Cd enriched soils (geochemical anomalies) such as the at least 50,000 year old California soils described by Bureau (1980) and Lund et al. (1981), and the old New York peat bog described by Cannon (1955) and Cannon and Anderson (1971). (107)

The annual vs cumulative effect of Cd was summarized in CAST 1980. This question may now be settled by the work of Mahler and Ryan (1982) who found that historic sludge applications caused a persistent increase in Cd sorption capacity, hence decrease in Cd uptake by crops. The slope of Cd concentration in chard or corn leaves vs newly added sludge or salt Cd was strongly reduced in previously sludged soil compared to the control non-sludged soils. It appears that organic (Seen, 1981) and inorganic (Singh, 1981) materials in sludge can provide the specific Cd sorption sites. This information indicates that the "time bomb" (Beckett and Davis, 1979) effect predicted to occur after sludge organic matter is stabilized in soil has no basis. (108) (43)

Further, Dowdy et al. (1981) deduced a new method to evaluate the separate contribution of annual and cumulative applied Cd. ~~Since annual Cd is a part of the true cumulative Cd, these dependent variables are co-variant; by using Cd applied up to the year before the present crop (lag cumulative Cd) they could use multiple regression analysis.~~ Their study showed that cumulative Cd dominated over the effect of annual Cd on Cd uptake to corn ear leaf or silage. ~~Please recall that the presence of organic and inorganic (salts, NH_4^+) ligands in freshly sludged soils can contribute to the apparent "annual" Cd effect.~~ (110)

The recent report of Chaney et al. (1982) shows that sludge Cd concentration has a strong effect on potential Cd levels in plants grown in acid soils many years after the sludge was applied. They analyzed the results using orthogonal contrasts, and found that, in addition to linear Cd rate and soil pH, quadratic Cd rate also significantly affected Cd uptake by lettuce. The curves for lettuce Cd vs sludge-applied Cd were not linear, but had much lower slopes after the first sludge Cd increment. This effect was clear for both sludges with 13 mg Cd/kg and 200 mg Cd/kg, but was especially important for the lower Cd sludge. The use of linear regression is clearly contraindicated. Using slopes for plant Cd vs soil Cd from experiments with high Cd sludges, Cd salts, or Cd-salt amended sludges should no longer be acceptable in estimating risk from recommended practices with low Cd sludges.

Many scientists have argued that farmers should accept only low Cd sludges because the cumulative applied sludge benefit is inversely related to sludge Cd concentration. The above research indicates that equal Cd applied in low or high Cd concentration sludges will cause unequal effect on Cd in crops. Actually, in research to settle the questions discussed above, it appears that experimental results were confounded by the factors discussed. In order to apply higher Cd rates, high Cd sludges were needed. Usually, experiments showing high Cd uptake used high Cd rates, high Cd concentration sludges, and high Cd:Zn ratio sludges.

Many experiments using low Cd, low Cd/Zn sludges have found low Cd in plants (Dowdy and Larson, 1975; Dowdy et al., 1978; Chaney et al., 1978a, 1982; Schauer et al., 1980; Harris et al., 1981; Giordano et al., 1979; Zwarich and Mills, 1982; deVries and Tiller, 1978; Sommers, 1980; Webber et al., 1981a; Chang et al., 1982; Lutrick et al., 1982; Sheaffer et al., 1981; Anderson and Nilsson, 1976; Gestring and Jarrett, 1982).

The effect of sludge metal concentration is also seen for other elements. A recent paper by Gupta and Haeni (1981) indicates that sludge Cu concentration greatly affected Cu uptake and phytotoxicity from equal Cu applications (hence unequal sludge applications). This paper supports earlier indications that potential phytotoxicity of sludge Zn, Cu, and Ni is related not only to metal application rate, but also to sludge metal concentration (Webber et al., 1981b; Marks et al., 1980). As expected, sludge-applied Zn, Cu, and Ni persist in their plant availability, at least in acid soils (Berrow and Burridge, 1981; Chaney et al., 1982; Marks et al., 1980; Williams, 1980).

METAL INTERACTIONS AFFECTING Cd LEVEL IN CROPS

The additivity of phytotoxic metals was reviewed above. Besides phytotoxic interactions, interactions affecting Cd concentration in edible plant tissues are also very important. In 1973, Chaney suggested that limitation of Cd:Zn ratio in sludges could limit crop Cd to acceptable small increases or Zn toxicity would result. He initially based this on the parallel increase of Cd and Zn in crops as sludge rate increases or soil pH declines, and on already known interactions of Cd and Zn in animals.

For vegetable crops, this interaction now appears to satisfy the claims of Chaney (1973, 1980). Chaney and Lloyd (unpublished) amended *Sassafras* sl with Cd and Zn sulfates and added CaCO_3 as needed to maintain equal soil pH. Romaine

lettuce was grown for 6 weeks, and analyzed. Selected results are shown in Table 6. Lettuce yield was substantially reduced at 400-to-500 $\mu\text{g/g}$ Zn in total leaves. At intermediate Zn levels, added Zn reduced crop Cd concentration, and crop Zn concentration was reduced by added Cd. However, the Cd concentration in healthy edible young lettuce leaves (those grown after transplanting) was constrained to about 4 $\mu\text{g/g}$ by either 1) Zn phytotoxicity, or 2) remaining within the recommended 1.0% Cd:Zn ratio (1.5% maximum on private cropland).

Related experiments were conducted by Hortenstine (1980) with lettuce and radish and Webber (1980) with lettuce, with similar results, although soil pH was not equal among treatments. ~~Often small additions of Zn increase Cd movement to shoots, while higher Zn reduced foliar Cd (Haghiri, 1974). Chaney et al. (1978) confirmed Haghiri's findings with soybean foliage, but found that Cd movement to soybean grain was strongly inhibited by increased Zn. Grain Cd:leaf Cd ratio fell from over 1 to less than 0.1 as soil Zn increased. Unfortunately, monocots do not appear to follow this pattern (cots - Chaney and White, unpublished; wheat - Bingham et al., 1979; rice - Bingham et al., 1980). However, movement of Cd to grain of monocots is not very great under present EPA (1979a) regulations. The greater tolerance of monocots to Zn in acidic soils could theoretically allow small grains with 2-5 $\mu\text{g/g}$ Cd; however, dicots in rotation would indicate the pH mismanagement by phytotoxicity and lead to limestone application.~~

Interactions between Zn and Cd in the intestine are discussed later in this paper. It is quite clear now that all or at least part of the small increase in crop Cd achievable under a Cd:Zn ratio limitation can be counteracted by the increased plant Zn.

Although the above research was conducted with metal salts, or metal salt-amended sewage sludge, the parallel increase of Cd and Zn is apparent in several research studies in which low metal sludges were applied to acid soils. For foliar Cd to exceed a few $\mu\text{g/g}$, plant Zn approaches phytotoxic levels, (Chaney et al., 1978a, 1978b, 1982; Zwarich and Mills, 1982; Gestring and Jarrell, 1982; Dowdy and Larson, 1975). The Cd:Zn ratio limitation was meant to add additional protection under the conditions where soil pH was poorly managed. The EPA (1979a) regulations adequately restrict metals in vegetable crops in soil at pH 6.5 or above.

METAL ACCUMULATIONS BY ANIMALS AND THEIR EFFECTS

PATHWAYS FOR TRANSFER OF METAL TO THE FOOD-CHAIN

Sludges are applied to land in many fashions. These management options allow substantially different amounts of sludge-borne metals to enter the food-chain, by different routes. High exposure can come through ingestion of sludge-covered forage by livestock, while mixing sludge into the soil uses reactions in soils and properties of plants to largely prevent exposure.

Sludge Adherence to Forage Crops

It is now generally recognized that spray-applied liquid sludges form a thin film covering crop foliage and, if not removed immediately by rainfall or irrigation, dry and adhere strongly (Chaney and Lloyd, 1979; Jones et al., 1979;

Bertrand et al., 1981). Sludge adherence is directly related to solids content of the applied sludges, and to sludge application rate. Growth of crop biomass dilutes the sludge percentage in harvested forage.

Digested sewage sludge has adhered to all crops studied, although crops do differ in relative adherence due to differences in structure and growth habits. Adherence is easily characterized because levels of many elements (Cu, Pb, Cr, Fe) in/on sludge-contaminated forages are much greater than levels ordinarily possible by uptake-translocation by plants. Many reports on uptake of microelements from surface-applied sludges have presumed uptake when sludge adherence fully explains the observations.

Another possible route of entry to food-chain is through farm equipment. Dalgarno and Mills (1975) reported that baled hay was enriched in Cu above levels found in/on the sampled forage crop. They presumed that the baling equipment lifted high Cu swine manure from the soil surface (or possibly the thatch layer). This route is poorly demonstrated. Silage can also contain soil, and the soil can interfere with microelement availability (Lamand, 1979).

When increased levels of microelements in forage indicate sludge adherence, all constituents present in the sludge contaminate the forage. Not only microelements, but also macroelements, pathogens (Brown et al., 1980) and toxic organic compounds (Fitzgerald, 1978) are increased.

Ingestion of Sludge-Amended Soil or Sludge From the Soil Surface

Grazing animals consume soil as part of the normal grazing process. This was noted initially during study of the excessive wear of teeth of sheep and cattle. Using soil Ti (not appreciably absorbed by plants) as an indicator/tracer on soil in feces, Healy et al. (1974) found that wet weather and excessive stocking rates caused forages to be trampled into the soil and increase soil adherence and ingestion. Although soil is normally only 1-2% of sheep's diet, soil could reach 24% in worst cases.

Mayland et al. (1977) reported that cattle grazing dryland-grown crested wheat grass consumed considerable quantities of soil. Because the cattle ate the plants complete with soil-laden roots, the ingested diet contained 20% soil. Fries (1982) recently reviewed soil ingestion by dairy cattle. Under good management, soil seldom exceeds 3% of dry diet.

Sewage sludge or composted sludge can be ingested from the soil surface. Decker et al. (1980) estimated that cattle grazing tall fescue pastures fertilized with sludge compost consumed 3.2% (1977) and 1.0% (1978) compost (of dry diet) based on fecal analysis. Compost did not adhere to the plant but lay on the soil surface.

Soil/sludge ingestion can also expose humans to applied microelements. Some children and adults deliberately consume soil in a practice called "pica." If the soil is rich in Pb (over 500-1000 $\mu\text{g/g}$), individuals may absorb excessive Pb (Wedeen et al., 1973; Shellshear, et al., 1975; NRC, 1980a). Children also inadvertently ingest soil and dust due to hand-to-mouth play activities, and mouthing of toys,

diets. When the animal performance was unaffected, some explanation was needed.

Evaluation of the potential risk to animals of sludge-applied microelements is very complex. Animal species differ in tolerance. Tolerance is influenced by age, with younger animals generally more sensitive. Total and relative element concentration is affected by crop species and cultivar, plant age, soil pH, soil organic matter, soil temperature, and other factors. Sludges differ in levels of elements and ratios among elements which interact in the animal. Particular toxic elements interact with other elements in the diet, often reciprocally. Because these interactions are often the basis for observed toxicity, interactions are very important in assessing risk of sludge-applied microelements.

Chaney (1983b), has provided a detailed discussion of exposure, interactions which affect risk, etc., for the principal metals in municipal sewage sludge (see summary in Table 7). Interactions are especially important in allowing or preventing toxicity of ingested Cu, Mo, Fe, Zn, Cd, etc.

"Domestic" low metal sewage sludge contains a mixture of potentially toxic elements. When sludge is ingested, ~~increased dietary Zn is balanced by normal or high levels of Cu and Fe.~~ Increased Cu is balanced by Fe and Zn which reduce Cu toxicity in ruminants. Although many thought high Cu swine manure would poison Cu-sensitive sheep based on "toxicology" studies, manure Cu has not poisoned sheep in feeding or grazing studies (Bremner, 1981; Poole, 1981). Sewage sludge ingestion has not even caused Cu accumulation in liver of cattle fed sludge (Kienholz, 1980; Edds et al., 1980; Smith et al., 1979; Decker et al., 1980) unless sludge Cu was high (Baxter et al., 1980; 1982). Low Cu, high Fe sludge allowed Fe-induced Cu-deficiency in cattle grazing tall fescue pastures (Decker et al., 1980). Thus, "Environmental Toxicology" research can lead to very different risk estimates than traditional toxicology.

~~ACCUMULATION BY ANIMAL ORGANS~~

(119)
Animals have homeostasis mechanisms for most elements (Underwood, 1977). High dietary Zn, Cu, Mn, Ni, Fe, etc. increase intestinal and liver concentrations of the element, but have little effect on other tissues. When feeding of the enriched diet ceases, tissue levels return to normal. Pb can build up in bone and kidney in forms slowly released. Inorganic Hg can build up in liver, and organic Hg in fat deposits and nerve tissue in forms slowly released. F can build up in bone as fluorapatite, a form slowly released. Cd can accumulate in liver and kidney in the form of metallothionein; Cd has the longest biological half-life of the elements of concern in sludge (about 20 years in humans).

~~POTENTIAL EFFECTS OF SLUDGE-BORNE CADMIUM IN THE FOOD-CHAIN~~

In 1973, relatively little was known about Cd in food and risk to humans. The occurrence of Cd-disease in Japan had just been announced. Toxicologists still thought hypertension could be caused by Cd. Food specialists thought we were nearly at the safe maximum daily Cd intakes based on meager knowledge of Cd toxicology and poor analytical data. Accumulation in animal organs is often the basis for regulations regarding sludge utilization.

Research on Cd risk has been especially intense because of these fears. From this research, a much more complete understanding of Cd risk has developed. Unfortunately, many scientists are not aware of the shift in our understanding about risk of sludge-borne Cd to humans in the U.S. Thus, the following is a more detailed review than some other portions of this paper.

Cd Exposure and Health Effects

Cadmium is an unusual and difficult case for evaluation of risk to the food chain. In contrast to other elements, Cd has a quite long biological half-life in humans--generally considered 20 years. Absorbed Cd is bound to a low molecular weight protein to form metallothionein which is accumulated and retained in the kidney for a long period. High metallothionein-Cd in the kidney can lead to adverse health effects in the kidney.

Over one's lifetime, chronic food chain Cd exposure can cause different health problems than those experienced from acute exposure. Long-lived animals (e.g., humans) are at greater risk of this chronic exposure health effect than are short-lived animals (wildlife; domestic animals). Accumulation of Cd in organ meats (liver, kidney) was the basis for suggesting a low dietary Cd tolerance in domestic animals rather than a direct health effect to the animals (NRC, 1980b).

The potential risk of excess soil Cd to humans has been clearly documented. Adverse health effects resulted from prolonged consumption of foods grown locally on Cd enriched soils (Tsuchiya, 1978; Friberg et al., 1974; Hammons et al., 1978; Kobayashi, 1978; Nogawa, 1978). A large number of Japanese farmers suffered Cd health effects after long-term ingestion of Cd-enriched rice grown in paddies polluted by Zn- and Pb-mining wastes or Zn-, Pb-, and Cu-smelter emissions in at least 7 different areas of Japan (Kobayashi, 1978; Takijima and Katsumi, 1973; Shigematsu et al., 1979; Kjellstrom et al., 1977; Kojima et al., 1979; Saito et al., 1977; Nogawa, 1978; Nogawa and Ishizaki, 1979; Nogawa et al., 1975; 1978; 1980; 1981). The farm families consumed their own rice due to cultural factors and tax policy. Rice Cd concentration and number of years exposure were both strongly related to the incidence rate of Cd health effects. A smelter enriched area in Belgium may have caused Cd-induced renal disease (Roels et al., 1981a) although route for exposure and increased kidney Cd have not yet been demonstrated.

The name "itai-itai" disease (translated as ouch-ouch disease) came from expressions of pain by women suffering repeated bone fractures due to Cd-induced osteomalacia. Although the osteomalacia brought attention to this environmental Cd disease, severe osteomalacia does not frequently result in humans ingesting excessive Cd; osteomalacia appears to result in Cd-exposed individuals only when dietary Ca is low. Renal proximal tubular dysfunction (Fanconi syndrome) is the first health effect of excessive chronic Cd exposure. The renal disease had high incidence in areas where Cd exposure was increased, and showed a dose-response relationship with Cd exposure (expressed as "Cd level in rice-times-years ingested"). All individuals with advanced itai-itai disease had severe proteinuria characteristic of the kidney disease. Renal disease subsequently proceeded to mild osteomalacia in some European workers who ceased exposure when the kidney disease was identified (Kazantzis, 1979). However, this aspect of Cd disease is poorly understood. Sub-clinical osteomalacia is found in many of the Japanese

farmers who experience renal disease but not "itai-itai" disease (Mukawa et al., 1980).

Renal tubular dysfunction (Fanconi syndrome) resulting from Cd ingestion is quite different from classic kidney failure. Fanconi syndrome seldom proceeds to kidney failure requiring dialysis. Kjellstrom (1978) indicated that Fanconi syndrome (low molecular weight proteinuria, glucosuria, aminoaciduria, phosphaturia, etc.) is the first Cd health effect; if Cd-exposure (rate-times-duration) is increased, kidney stones and osteomalacia/osteoporosis may result. Kjellstrom et al. (1979) found greater mortality (shorter life span) in Cd exposed workers. Nogawa et al. (1981) found significantly greater mortality risk in farmers with proteinuria. Neither hypertension nor prostate cancer incidence are increased even when proteinuria is severe (Friberg et al., 1974; Doyle, 1977; Hammons et al., 1978; Tsuchiya, 1978; Ryan et al., 1982; Commission of the European Communities (CEC), 1978; Kjellstrom and Nordberg, 1978; Kjellstrom et al., 1979; Lauwreys et al., 1980; Nogawa, 1978; Nogawa et al., 1981; Shigematsu et al., 1979). Although Kopp et al. (1982) claimed that hypertension in Cd-fed rats indicated risk to humans at current dietary exposure levels, the dose rates they fed expressed on the basis of 70 kg adults (700-1400 µg/d) are high enough to have caused Fanconi syndrome. Although laboratory studies with rats and other animals have shown that anemia, enteropathy, and teratogenesis (due to Cd-induced Zn or Cu deficiency in the fetus) can result from ingested Cd, these are very unlikely with practical diets or with crops fertilized with low Cd sludges.

A number of researchers and groups have attempted to clarify the dose-effect and dose-response relationships for Cd (CEC, 1978; Friberg et al., 1974; Kjellstrom and Nordberg, 1978; Ryan et al., 1982; Tsuchiya, 1978). The first sign of renal tubular dysfunction (increased excretion of B₂-microglobulin or retinol binding protein, a specific proteinuria characteristic of Cd injury) is generally agreed to occur at about 200 mg Cd/kg wet kidney cortex. Some research indicates that the critical kidney cortex Cd level may be as high as 300 mg/kg (Roels et al., 1981b; Ellis et al., 1981), but 200 mg/kg is the level generally accepted for use in risk analysis. Individuals may vary about this population estimate.

Kjellstrom and Nordberg (1978) developed a sophisticated multicompartamental dose-effect model for Cd metabolism in humans: "This present model predicted that a daily intake corresponding to 440 µg at age 50 would give 200 µg Cd/g of (wet) kidney cortex at age 45-50." These results were obtained by assuming a high, constant Cd concentration per unit calories, and that calorie (hence Cd) ingestion varied with age in the manner of the average diet of the Swedish population. The "best fit" calculated 4.8% lifetime average absorption of dietary Cd, 440 µg Cd/d at age 50, and a 12 year biological half-life for Cd to achieve the 200 µg Cd/g wet kidney cortex at age 45-50.

Other researchers have used different ways to express Cd-exposure information, thus complicating interpretation of results from these many sources. In the U.S., the Food and Drug Administration (FDA) has measured food Cd concentrations and average Cd ingestion (FDA, 1977). Food consumption was based on USDA's 1965 dietary intake survey but adjusted to a "balanced" diet; FDA, USDA, and EPA agreed to use a food consumption model based on teenage males (highest food consuming group) in a pesticide residue survey program. Thus, for the

same food supply, a mean food Cd ingestion of 39 $\mu\text{g/day}$ from FDA corresponds to about 23 $\mu\text{g/day}$ intake at age 50 in Kjellstrom and Nordberg's (1978) model. Their model reflected 3430 kcal/d for Swedish teenage males vs. 2045 kcal/d for 50-year-old Swedish individuals (Fig. 4.32 and 4.34 in Friberg et al., 1974). Thus, the critical 440 $\mu\text{g Cd/day}$ ingestion rate for 50-year-old individuals in Kjellstrom and Nordberg's (1978) model corresponds to approximately 738 $\mu\text{g Cd/d}$ ingestion in U.S. teenage male diets. The present average exposure is only 5.2% of the critical exposure (23 vs 440 or 39 vs 738).

Chaney (1983b) and Ryan et al. (1982) discuss difficulties in interpreting dose-response relationships for dietary Cd. Individuals vary widely in self-selected diet and dietary Cd (Yost et al., 1980), in Cd absorption rate (Flanagan et al., 1978; McLellan et al., 1978), and in sensitivity to absorbed Cd. These phenomena are generally assumed to vary in a log-normal fashion in a population. Kjellstrom (1978) extended the 440 $\mu\text{g/d}$ model "critical" level to a population by arbitrarily using a geometric standard deviation of 2.35 based on studies of Cd in autopsy tissues (see Ryan et al., 1982 for details). However, Kjellstrom's (1978) model would require greater than 100% absorption of dietary Cd by the most sensitive individuals (see Figure 1 in Chaney, 1980). The highest Cd absorption rate observed for humans is 25% reported by Flanagan et al. (1978) for a woman with mild anemia; Fe stress strongly increases Cd absorption. Several researchers (Chaney, 1980; Ryan et al., 1982) argued that it was unreasonable to extrapolate the 440 $\mu\text{g Cd/d}$ "Average Human" model result to an assumed maximum sensitivity group with greater lifetime percent absorption of Cd than ever observed in humans. Further, individuals are unlikely to be in this greatest risk group for their whole lifetime.

Thorough analysis of the Cd injury of Japanese farmers conducted during the last decade appears now to support only a dietary threshold type dose-response curve. For any individual to be injured, sufficient Cd must have accumulated in the kidney to induce proteinuria. Although individuals vary in retention of dietary Cd, and in kidney Cd associated with initial low-molecular-weight proteinuria (LMW-proteinuria), much Cd must be consumed to reach this condition. Food Cd must exceed some level before the most sensitive individuals experience LMW-proteinuria.

The Japanese data indicate that, for individuals over 70 years of age, incidence of LMW-proteinuria was not significantly increased until rice Cd exceeded 0.40 $\mu\text{g/g}$. For individuals 50-60 years of age, incidence of LMW-proteinuria was not significantly increased until rice Cd exceeded 0.60 $\mu\text{g/g}$. Individuals are presumed to have eaten 300 g rice/day; thus acceptable exposure was $300 \times 0.4 = 120$ $\mu\text{g Cd/d}$ for persons over 70 years old, and $300 \times 0.6 = 180$ $\mu\text{g Cd/d}$ for 50-60 year old's. The standard Japanese is considered to weigh 53 kg (Kjellstrom, 1978), while the standard Westerner is considered to weigh 70 kg. Adjusting for this difference, the first significant observation of LMW-proteinuria in U.S. citizens should require 238 $\mu\text{g Cd/d}$ for a 50 year model, or 158 $\mu\text{g Cd/d}$ for a 70 year model. These analyses disregarded Cd exposure from smoking which would have increased daily intake above that from rice. Thus, the log-normal extrapolation appears inappropriate compared to the threshold model (Ryan et al., 1982).

Ryan et al. (1982) concluded that a 200 $\mu\text{g/d}$ (150 $\mu\text{g/d}$ after protecting smokers) threshold model (based on average lifetime daily Cd intake) of individuals

was more appropriate for dose-response considerations, as did the CEC (1973) workgroup. This value corresponds to about 14.1% lifetime Cd absorption rate for the most sensitive individuals [4.8(440/150)].

Cd Bioavailability

Cadmium absorption by animals is strongly influenced by other dietary factors (Fox, 1976, 1979; Fox et al., 1978, 1979; Jacobs et al., 1978a, 1978b, 1983; Flanagan et al., 1978; Welch et al., 1978; Welch and House, 1980; Kostial et al., 1979; Cousins, 1979; Kobayashi, 1978; Washko and Cousins, 1977). Iron status of the animal appears to be the most important control of percent absorption of Cd and many individuals ingest low Fe during at least part of their life. Zinc status of the animal and dietary Zn level is the next most important factor, followed by dietary Ca. Protein and fiber in the diet and age of animal also influence Cd retention. These factors should allow a greater percent absorption rate for women than men. Women as a group showed greater Cd absorption (Flanagan et al., 1979), and women's kidney Cd exceeds men's in autopsy kidney studies, as did women's susceptibility to excessive dietary Cd in Japan.

Dietary interactions can thus influence bioavailability of Cd. Leafy and root vegetables which are enriched in Cd may also be a good dietary supply of Zn, Fe, and Ca. Leafy vegetables have been shown to provide bioavailable Fe and Zn (Welch et al., 1977, 1978; Van Campen and Welch, 1980; Wien et al., 1975). Chaney (1980) suggested that leafy and root vegetables grown on soils enriched in Cd from being fertilized by low Cd, low Cd:Zn sewage sludges comprise a separate risk scenario. In this case, consuming sufficient food Cd to pose a risk to individuals susceptible because of nutrition status would result in increased dietary Fe, Zn, and Ca, thereby shifting the individuals to a less susceptible population group.

~~Feeding studies have been conducted with sludge and with crops grown on sludge-fertilized soil.~~ Ingestion of ~~sludge Cd~~^{Cd} has been evaluated in ruminant and monogastric animals, with most work done with cattle. When sludges with high Cd and high Cd:Zn were fed, kidney Cd was significantly increased (Kienholz, 1980; Baxter et al., 1980, 1982; Hansen and Hinesly, 1979; Hinesly et al., 1976, 1979a; Edds et al., 1980; Fitzgerald, 1980; Lisk et al., 1982; Johnson et al., 1981). However, when sludges with lower Cd and low Cd:Zn were fed, kidney Cd was not significantly increased (Decker et al., 1980; Kienholz et al., 1979; Kienholz, 1980; Baxter et al., 1980; Bertrand et al., 1981; Edds et al., 1980; Smith et al., 1979). Sludge Cd was less bioavailable to swine than equal Cd added as CdCl₂ (Osuna et al., 1979; Edds et al., 1980). Food products of animals are unchanged in Cd except for liver and kidney (e.g., Sharma et al., 1979). Kienholz (1980) noted that dietary interactions could avoid even this impact of sludge Cd. Thus, risk analysis for ingested sludge Cd requires evaluation of several factors other than dietary Cd concentration.

As noted above, the Cd-injured Japanese farmers were deficient in several nutrients (Ca, Zn). Rice was the source of nearly all the increased dietary Cd. Although the soils contained both Cd and Zn (at Cd:Zn about 1:100) from mining wastes, the rice was increased in Cd but not Zn. Rice grain grown under flooded culture contained only 20-25 µg/g Zn while rice Cd rose from normal levels of 0.05 µg/g to over 2 µg/g (page 237 in Tsuchiya, 1978); polished rice is very low in Ca and Zn.

~~Similarly,~~ Risk analyses for ingestion of Cd in foods grown on Cd-enriched soils requires careful evaluation of factors other than Cd. Far too little research has been conducted to characterize bioavailability of food Cd. Further, very little of the completed research conforms with the experimental designs which Fox et al. (1978, 1979) and Fox (1976) indicated were needed to allow interpretation. Dietary Cd level should correspond to the range of nutritional relevance to humans. Intrinsically Cd labelled foods should be fed in the state ordinarily ingested by humans (e.g., fresh leafy vegetables). Nutritional status of the experimental diet should be adequate for all known essential factors or varied as part of the experiment. The feeding period should be of sufficient length to allow nutritional status of animals to be under control of experimental diet for the bulk of the experimental period. Several animal species should be studied. Bioavailability of Cd in a food or a sludge-grown food can only be determined experimentally.

The bioavailability of Cd may also be influenced by the chemical species of Cd present in crops. Several studies have reported the existence of an inducible protein which can bind Cd in plants (Bartolf et al., 1980; Weiger and Jager, 1980; Wagner and Trotter, 1982; Casterline and Barnett, 1982). Unfortunately, these studies used phytotoxic levels of Cd in their research. It is possible that high levels of Zn or other metals might also affect the chemical species of Cd in edible plant portions. Thus, research is needed on potential shifts in chemical species of Cd in sludge fertilized crops and its effect on Cd bioavailability, if any.

~~Cd in Tobacco~~

Tobacco is an especially high risk crop in terms of potential for Cd effects on humans. Among all crops studied to date, tobacco accumulates more Cd per unit soil Cd than any other (Chaney et al., 1978a; Maclean, 1976; Davis and Carlton-Smith, 1980). In many areas, tobacco is normally grown on strongly acid soils to prevent crop loss from root diseases. This soil pH management leads to maximum Cd uptake under normal crop production conditions. In contrast, most other crops are best grown at pH 6.5 to 7. Tobacco is normally high in Cd compared to leaves of other crop plants, and high leaf Cd levels in some production areas are being studied (Frank et al., 1977; Westcott and Spincer, 1974). When tobacco is grown on acidic sewage sludge-amended soils, crop Cd levels can be increased from 1 to as high as 44 µg/g Cd in dry leaves (Chaney et al., 1978a) with only 1 µg/g soil Cd. Gutenmann et al. (1982) applied 19 kg sludge Cd/ha and found tobacco Cd increased from 3.2 to 67.4 µg/g.

NOTE: Cadmium in tobacco is an important source of Cd for humans. Individuals who smoke one pack of cigarettes per day have about 50% higher Cd in kidney cortex than non-smokers (Lewis et al., 1972; Elinder et al., 1976). About 15% (5-25%) of cigarette Cd enters the mainstream smoke (Szadkowski et al., 1969; Menden et al., 1972; Westcott and Spincer, 1974). Filters can remove much of this Cd and reduce Cd exposure of smokers (Westcott and Spincer, 1974; Franzke et al., 1977). Based on the potential of sludge-applied Cd to increase risk of chronic kidney disease in smokers if sludge were applied to tobacco cropland, EPA (1979) regulated and discouraged this practice. Some tobacco growing states have even prohibited sludge applications on land suited for tobacco production. (19)

Models for Limits on Cd Application

Several food crops are of especial importance to evaluating Cd-risk for humans. While grains supply much Cd to individuals in the general population (~~Braude et al., 1976; Jelinek and Braude, 1978; Ryan et al., 1982~~), individuals are extremely unlikely to grow a significant portion of their food grains. Rather, individuals are likely to grow leafy and root vegetables, legume vegetables, garden fruits, and potatoes. If the Cd:Zn ratio of an acidic Cd-enriched garden soil is high, edible crop tissues of leafy, root, and legume vegetables, garden fruits, and potatoes can be greatly increased in Cd concentration with no injury to the crop and provide excessive bioavailable Cd. If the Cd:Zn ratio of an acidic Cd-enriched garden soil is low (< 0.01), these crops are not greatly increased in Cd when Zn phytotoxicity limits crop yield, (see data for lettuce in Table 5), and bioavailable Cd would be only slightly increased. The difference in risk from low Cd:Zn and high Cd:Zn gardens is due to: 1) Zn-phytotoxicity at low pH in the low Cd:Zn garden causing the gardener to add limestone which reduces crop Cd or have little yield (hence, reduced exposure), 2) interactions between Cd and Zn in plant uptake and translocation to edible plant tissues (~~Chaney et al., 1976; Chaney and Hornick, 1978~~); and 3) interactions in the diet which influence Cd bioavailability.

It is much more difficult to evaluate Cd bioavailability from foods grown on waste-amended soils than from Cd-amended purified diets. Freeze-dried lettuce and chard grown on acidic soils amended with domestic sludge were fed at a high percentage of diet to mice or guinea pigs (~~Chaney et al., 1978b, 1978c~~). Although dietary Cd was increased by up to 5-fold by lettuce or chard grown on acidic, domestic sludge-amended soil, kidney Cd was not increased. Bertrand et al. (1980) found similar results for forage. In other studies with high Cd and/or higher Cd:Zn sludges, feeding sludge-grown crops has caused increased kidney Cd (~~Chaney et al., 1978b; Miller and Boswell, 1979; Heffron et al., 1980; Lisk et al., 1982; Telford et al., 1982; Williams et al., 1978; Hinesly et al., 1976, 1979~~).

A recent paper by Boyd et al. (1982) shows another difficulty of assessing risk of sludge-applied Cd. They applied 8.6 kg Cd/ha in one 112 Mt/ha application (violated 5 kg Cd/ha and 0.5 kg Cd/ha/yr limits of EPA, 1979a). However, snapbean and squash absorbed little increased Cd, and kidney Cd was equal to control or decreased (Table 8). Sludge-fertilized cabbage and redbeets were six times higher in Cd than control crops, yet kidney Cd was increased less than two-fold. Thus, sludge Cd had little effect on kidney Cd when vegetable crops were grown, even though Cd regulations (annual and cumulative Cd for acid soils) and recommendations (sludge Cd < 25 $\mu\text{g/g}$ and Cd/Zn < 0.015) were exceeded. Two other cabbage feeding studies failed to meet "Environmental Toxicology" standards (cabbage grown on 1.2 m deep pile of high Cd sludge, and fed at 30% of diet to rats or 45% of diets to sheep); reported kidney Cd increases are thus irrelevant to sludge risk analysis (~~Waschek et al., 1979; Babish et al., 1979~~). Clearly, more sludge-soil-plant-animal studies are needed to characterize the bioavailability of Cd in crops grown on waste-amended soils. It seems very likely that factors besides background soil pH, and annual and cumulative Cd application will eventually have to be considered in setting allowed Cd loadings on cropland (EPA, 1979a; Chaney et al., 1980a). ~~It is probable that general limited accumulation of Cd in "backyard" garden plots (19) may be maintained by the use of low Cd sludges and/or by the use of protective~~

For the purpose of this study, 38

TABLE 8. CADMIUM AND ZINC IN EDIBLE CROP TISSUE AND KIDNEY OF RATS FED FOUR CONTROL AND SLUDGE-FERTILIZED CROPS FOR 84 DAYS (Boyd et al. 1982)

Crop	Crop Analyses				Kidney Analyses			
	Cd, $\mu\text{g/g dry}$		Zn, $\mu\text{g/g dry}$		Cd, $\mu\text{g/g dry}$		Zn, $\mu\text{g/g dry}$	
	C*	S	C	S	C	S	C	S
Beans	0.1	0.1	30	34	3.4	1.1	89	90
Squash	0.2	0.3	15	54	4.9	3.8	100	86
36 Cabbage	0.2	1.3	17	93	7.1	9.7	80	103
Redbeets	0.5	3.2	27	125	5.4	12.6	83	95

* C and S denote control and sludged, respectively. Applied 112 dry Mt/ha of sludge containing 77 mg Cd and 3477 mg Zn/kg, applying 8.6 kg Cd/ha.

Much of the potential risk from Cd in waste-amended soils has now come under regulation in the U.S., although these regulations do not have to be enforced until September, 1984. The highest risk case, application of sludges to gardens as fertilizers or soil conditioners, has not yet been regulated (Comptroller General, 1978; Chaney et al., 1980b). Further, pretreatment of Cd-bearing industrial wastes, segregation of waste streams, and avoidance of Cd use for non-critical applications offer great opportunity to avoid all Cd health effects (Dage et al., 1979; Gurnham et al., 1979).

In the process of developing Federal regulations for land application of sewage sludge (EPA, 1979a), EPA prepared a "worst practical case" scenario relating sludge-applied soil Cd to potential for kidney dysfunction in order to protect the higher risk sensitive individuals (EPA, 1979b). The worst case which may occur appears to be the acid garden case. Although grain crops can absorb Cd, individuals in the U.S. do not grow their own food grain on acidic, Cd-enriched soils. Similarly, consumption of liver and kidney enriched in Cd from sludge utilization is a minor source of dietary Cd. This approach protects individuals with soils least able to keep Cd from reaching their foods.

Thus, the acidic garden scenario was used. It presumed that 1) the garden contains the full allowed Cd application, 5 kg/ha; 2) the garden is continuously acidic, about pH 5.5; 3) the gardener obtains 50% of his annual supply of garden vegetables from the acidic, sludge-amended garden, including potatoes, leafy, root, and legume vegetables, and garden fruits; 4) the individual eats these amounts of garden vegetables for 50 years from the acidic sludge-amended garden; and 5) the individual is part of the sensitive-to-cadmium portion of the population. Further, EPA used a normal Cd ingestion value of 39 $\mu\text{g/day}$, a value selected from the range of annual estimates (28-51 $\mu\text{g/day}$ during 1970-1979) of daily dietary intake of Cd obtained in FDA's Total Diet Studies. They subtracted this 39 $\mu\text{g Cd/d}$ for the teenage diet model from the 71 $\mu\text{g/d}$ WHO-FAO (1972) provisional daily Cd ingestion to obtain a maximum allowed increase due to sludge use. The WHO-FAO tolerable intake is for population average adult exposure. Fecal analysis indicates that U. S. adults ingest about 20 $\mu\text{g/d}$ (Kowal et al., 1979), and adjustment of the teenage diet to adult diet gives a similar estimate of 23 $\mu\text{g/d}$. Thus, this part of the EPA (1979a) rule offered another safety factor. Based on new dietary consumption research findings, FDA has recently revised the methods used to estimate consumption of contaminants in US diets (Pennington, 1983). Individual foods are analyzed (to avoid detection limit questions on food composites). Thus, dietary Cd ingestion can be estimated for 8 age-sex groups rather than only teenage males.

It appears now that several linked assumptions of EPA's acidic garden scenario may well be mutually exclusive, and provide excessive protection at least for "Domestic" sludges. First, individuals who grow 50% of their garden vegetables have such a large time and work investment in their gardens that they learn about the effects of acid soils on yield of vegetable crops, and carefully manage soil pH at 6.5 to 7. Second, presuming that a low Cd, low Cd:Zn ratio sludge supplied the soil Cd, and that soil pH declines slowly due to fertilizer use, phytotoxicity in sensitive crops will cause a "50% gardener" to learn about soil pH management and interrupt the necessary 50 year acid garden exposure. Third, vegetables supply microelements which counteract Zn, Fe, and Ca deficiencies; these deficiencies are the identified basis for sensitive individuals. Thus, consumption of the

vegetables which comprise the minimal Cd risk to sensitive individuals in the EPA scenario (71 $\mu\text{g/d}$) may push them out of the sensitive population. Recall that increased Cd in "domestic" sludge-grown chard and lettuce did not cause increase in kidney Cd (Chaney et al., 1978b, 1978c). Alternatively, the presence of higher levels of other elements may have simply changed Cd speciation in foods to a form with lower bioavailability. In their discussion of Cd dose-response models, Ryan et al., (1982) concluded that U.S. sensitive individuals are protected at the 150 $\mu\text{g Cd/day}$ level of exposure ($150-20 = 130 \mu\text{g/d}$ vs $71-39 = 32 \mu\text{g/d}$). Alternatively, the FAO-WHO 71 $\mu\text{g Cd/d}$ value for adult diets may need to be adjusted from adult diet to teenage diet if the 39 $\mu\text{g/d}$ result is to be used ($=119 \mu\text{g/d}$, with $119-39 = 80 \mu\text{g/d}$ increase tolerable in teenage diet model).

Further, the slope of the crop Cd vs soil Cd relationship is strongly affected by sludge Cd concentration (Chaney et al., 1982); use of low Cd sludges gives appreciably lower slope (hence lower potential exposure at 5 kg Cd/ha regulated cumulative maximum Cd). The slopes for crop uptake from low Cd sludges are much lower than the slopes used in risk estimates (see EPA, 1979b; Ryan et al., 1982). High rates of low Cd sludges had little or no effect on Cd in major garden vegetable crops (Dowdy and Larson, 1975; Dowdy et al., 1978; Chaney et al., 1982; Harris et al., 1981).

Some scientists have expressed a concern that the safety factor for dietary Cd is small (e.g. Jelinek and Braude, 1978). The present review and Ryan et al. (1982) indicate that the safety factor is larger than previously believed. We believe that this new information is most responsibly used to demonstrate the existence of a larger safety factor when low Cd domestic sludges are utilized, rather than to support higher limits for Cd application on cropland. It remains clear that high Cd, high Cd/Zn sludges do not enjoy the improved safety factor shows for "Domestic" sludge. The larger safety factor should reduce public fear of recommended quality sludges. It provides greater protection of sensitive individuals who select diets with higher than average Cd content. As a result of these newer understandings, and in response to concerns expressed by the food industry, the regulatory and advisory agencies developed a policy statement on utilization of low Cd sewage sludge on cropland for production of fruits and vegetables (EPA-FDA-USDA, 1981).

In summary, the "Soil-Plant Barrier" does not protect the food chain from excessive Cd. Unregulated application of Cd-bearing wastes can cause health effects in humans. Cadmium is not easily kept out of food crops; conversion of treated land to gardens is a worst case scenario upon which regulations to limit Cd applications were based (EPA, 1979a). Recent research on gardens polluted with Cd by mining wastes or smelter emissions support the view that gardens can provide much Cd in locally grown foods to the family maintaining the garden for many years (Davies and Ginnever, 1979; Chaney et al., 1980, unpublished). Some aspects of the Cd-waste-soil-plant-animal food chain are not well established, and research is needed to avoid unnecessarily restrictive limits in the regulations. Recent research indicates that there is a substantial difference in potential risk from Cd in high Cd sludges vs. low Cd, low Cd/Zn sludges, and that for the "domestic sludge" case, the safety factor for dietary Cd is much larger than previously believed. The larger safety factor conclusion rests on: 1) Sensitive individuals are protected at 150-200 $\mu\text{g Cd/d}$; 2) adult US diets contain about 20 $\mu\text{g Cd/d}$; 3) Zn phytotoxicity can sharply limit maximum achievable crop Cd

levels; 4) Cd in crops grown on soils amended with low Cd, low Cd/Zn sludges has very low bioavailability; and 5) crop uptake of Cd per unit soil Cd is much lower for low Cd sludges.

~~POTENTIAL EFFECTS OF OTHER SLUDGE-BORNE ELEMENTS, ON THE FOOD-CHAIN~~

A few elements besides Cd have been of high interest or concern regarding risks from sludge utilization, and are considered briefly here. Other elements are not discussed here because they are low in sludges (As, etc.) or high levels are tolerated by animals (Cr^{3+} , Al, Sn, etc.). The discussion of soil-plant barrier above indicates that only a few elements merit the concerns expressed in 1973. Further, the special low risk case resulting from utilization of recommended quality sludges (Chaney, 1980) substantially alters the potential for risk from many elements in sludge.

Cobalt

Excessive dietary Co can cause toxicity in ruminant animals, while monogastric animals are more tolerant, (NRC, 1980b). ~~Diets with over 10 µg/g Co (as soluble salts) have injured cattle and sheep.~~

Unfortunately, plants tolerate higher levels of foliar Co than ruminants tolerate in their diets. Most plants show symptoms or substantially reduced yield at 50-100 µg/g Co in foliage (see Chaney, 1982b). However, no feeding studies have been conducted with plant-absorbed Co. Sludges are normally low in Co (Sterrett and Lester, 1981), and there is little reason for concern about sludge Co unless the sludge is high in Co.

Copper

Phytotoxicity due to excessive soil Cu occurs in most plants at 25-40 µg/g Cu (see Walsh et al., 1972). Copper toxicity in sensitive sheep and cattle occurs at 25-100 µg/g Cu (as soluble Cu salts). However, increased dietary Zn, Cd, Fe, or Mo would counteract added Cu, (Bremner, 1970, 1981) (68).

In order for crops to contain 25-40 µg/g Cu, they would have to be grown on acidic soils quite high in sludge. For the "Domestic" sludge case, these plants would have increased Zn which would prevent any toxicity due to the small possible increase in plant Cu. Similarly, ingested sludge and high Cu manures have caused no Cu toxicity problems even though dietary Cu reached 50 µg/g (Bremner, 1981; (147).
Peole, 1981).

Fluoride

Fluoride is normally low in plants because F is precipitated and/or sorbed strongly in soils. Sludges are normally low in F; 80% of sludges surveyed contained lower than 450 µg/g. However, a few sludges are very high in F, with the highest reported 3.35% F. Davis (1980) found that this high F sludge could temporarily cause increased F uptake by ryegrass. However, others have not found increased F in sludge fertilized plants.

Direct ingestion of sludge circumvents the soil-plant barrier for F. Kienholz et al. (1979) found increased bone F in cattle fed sludge with normal F concentration. Sludges surface-applied to pastures or forage crops should be analyzed for F and sludges high in F should not be surface applied on forages.

Iron

Iron is normally restricted to 40-300 µg/g dry foliage by plant and soil properties. Fertilizing with sludges, even sludges very rich in Fe, does not increase Fe appreciably above normal levels. Soil on contaminated forages often provides more total Fe than forage crops.

Although animals tolerate increased ferric iron, 1000 µg/g ferrous Fe added to forage diets reduced liver Cu in sheep and cattle. On low Cu diets, Fe can induce Cu-deficiency (NRC, 1980b). Fe-toxicity was observed in cattle grazing tall fescue pastures sprayed with a digested sludge containing 11% Fe (Decker et al., 1980). Sludges lower in Fe and sludge composts (ferric Fe) did not cause Fe-toxicity. When digested sludges are surface-applied to pastures, sludge Fe concentration should be analyzed. Sludges over about 4% Fe have caused Fe-induced Cu-deficiency; these observations were probably related to the crop, method of grazing, and low sludge Cu concentration (Chaney, 1983b).

Lead

Sludge applied Pb has been found to not increase plant Pb unless sludge Pb concentration is extremely high. Often, sludge application reduced plant Pb even though soil Pb is increased. This has been observed in all soil types, and for all crops studied -- grains, fruits, tuber and edible root, and even leafy vegetables. The reduced uptake may result from sludge-increased soil Pb sorption capacity, or phosphate which reduced Pb translocation within plants.

Although sludge-applied Pb, mixed in the soil, appears to comprise no potential risk in any scenarios presently used by regulatory agencies, new information is now available on risk to children ingesting moderately high levels of Pb. Classic Pb poisoning of children can cause an encephalitis which often leads to severe retardation. Ingestion of Pb-paint contaminated soils has caused excessive blood Pb in children with pica for soil. Recently, Needleman et al. (1979, 1980) have shown that a neurobehavioral impairment (lower IQ and school achievement, and problem classroom behavior) correlates with Pb concentration in deciduous teeth. Winneke et al. (1981) independently corroborated the Needleman group's finding. Thus, higher than normal Pb ingestion may be undesirable in children. Because some sludges may be surface applied as lawn fertilizers or mulches, their Pb concentration and its bioavailability may be important. Sludge Fe, P, Ca, and organic matter would reduce Pb absorption. It appears that "Domestic" sludges comprise no risk to livestock, or to human adults through plant uptake or soil ingestion (Chaney, 1983b). Research is needed to determine whether ingestion of small amounts of sludges low in Pb adds to Pb risk of infants and children (22).

Mercury

Mercury is noted for the food-chain poisoning resulting from methyl mercury accumulation by aquatic organisms which become human food. However, the

terrestrial ecosystem is quite different than the aquatic. Mercury is bound so strongly in soil and in plant fibrous roots that uptake by plants is not the limiting factor. Some volatilization of Hg vapor can occur when soils are rich in Hg.

Sludge Hg appears to be important in two sludge utilization cases. First, direct ingestion of sludge rich in Hg will increase liver Hg (Kienholz, 1980). Second, if sludges are used in the composts for mushroom production, mushrooms can exceed 0.5 µg Hg/g fresh weight, the level regulated in fish. Domsch et al. (1976) found excessive Hg in mushrooms grown on refuse-sludge compost. Frank et al. (1974) found even some horse manure is high enough in Hg to cause excessive mushroom Hg. Mushroom species vary widely in Hg and methyl-Hg accumulation (Stijve and Roschnik, 1974).

In research on production of mushrooms on composts including composted municipal refuse (Schisler and Grable, 1976), the excessive Hg accumulation observed by Domsch et al. (1976) was confirmed. Further, the Hg availability to mushrooms from refuse compost appears to be greater than that in traditional mushroom composts (L. C. Schisler, Pennsylvania State University, personal communication). Thus, sludge compost should not be used in mushroom production until research shows that Hg levels in the mushrooms will not exceed levels regulated by FDA.

Molybdenum

Excessive plant Mo can poison ruminant animals, but not monogastric animals under an enriched garden scenario. The ingested molybdate is converted to tetrathio-molybdate which can form an insoluble and unavailable compound with Cu. This causes a severe Mo-induced Cu-deficiency, a practical problem in sheep and cattle in many nations. Plants tolerate quite high levels of Mo without causing symptoms or substantial yield reduction. If forages contain 5-10 µg/g Mo, such that the Cu:Mo ratio falls below two, induced Cu deficiency can occur. In contrast to metal cations, anionic molybdate uptake by plants is increased as soil pH is raised. Most excessive plant Mo problems occur on calcareous soils. <

Sewage sludges are very seldom high in Mo, but a few were high enough to need study. Williams and Gogna (1984) reported Mo uptake by white clover and ryegrass grown on alkaline soil amended with sludges low (5 µg/g) or high (103 µg/g) in Mo, or with equal amount of molybdate. The high Mo sludge caused excessive Mo uptake by white clover; sludge Mo availability was approximately equal to that of molybdate. The low Mo sludge caused no appreciable change in plant Mo. Davis (1981b) reported Mo and Cu uptake by forage crops on soil from a sludge farm (515 µg/g Cu and 6.0 µg/g Mo). Clovers and brassica forages had unfavorable Cu:Mo ratios. He also reported the expected soil pH effect on Mo uptake from soils amended with a Mo-rich sludge. Based on these findings, sludges to be applied to neutral pH or calcareous soils for forage production should be analyzed for Mo to protect ruminant animals. (122).

Nickel

Nickel represents elements for which phytotoxicity completely protects the food chain. Ruminants tolerate at least 50 µg/g Ni (NRC, 1980b), while forage crops show visual symptoms of toxicity at 50-100 µg/g. Cattle suffered no effects

1-2
from forage diets with 250 µg/g Ni as NiCO₃, while soluble Ni salts caused the animals to reduce food consumption. Alexander et al. (1979) reported no toxicity or Ni bioaccumulation in meadow voles fed soybean grain containing 30 µg/g Ni, about the highest level possible without severe yield reduction.

Selenium

Although plant absorbed Se has poisoned livestock in several areas of the Western U.S. (Hobbs and Allaway, 1972), there is no reported indication that sludge-borne Se causes excessive plant or animal Se (Kienholz, 1980). Fly ash can cause excessive Se uptake if poorly disposed, or correct Se deficiency in livestock if used wisely (Gutenmann et al., 1979). Annual monitoring of sludge for Se can identify sludges with potentially excessive Se. Uptake of Se is favored on alkaline soils, or soils where Se-accumulator crops leave residues of seleno-amino acids.

Zinc

Excessive dietary Zn (300-1000 µg/g) can injure ruminant animals by inducing Cu-deficiency (NRC, 1980b). Sheep with low dietary Cu were injured when dietary Zn exceeded 300 µg/g (Campbell and Mills, 1979). Smelter Zn pollution injures horses, which are sensitive to excess. Gunson et al. (1982) reported erosion of cartilage in joints, a manifestation of severe Cu deficiency (Bremner and Campbell, 1980). However, Zn causes appreciable and/or visible injury to plants when foliar Zn is 500 µg/g (see plant uptake section). Sludge risk scenarios include strongly acid soils. Although high Zn sludges may be equivalent to Zn salts in risk scenarios, "Domestic" sludges apply Cu and other nutrients. Acid soil-grown forage crops would not be low in Cu or Fe; further, forage crops are not Zn-accumulators. Thus, livestock are protected from excess crop Zn problems when "Domestic" sludges apply the Zn. Sludge ingestion studies have found no Zn toxicity problems, likely due to the rich Cu and Fe supply in sludge. It is conceivable that ingestion of high Zn, low Cu sludges could lead to induced Cu deficiency in ruminants.

The acid garden scenario for Cd could be applied to Zn. Because leafy vegetables comprise such a small part of human diets, and because Zn is much lower in seeds, fruits, and edible roots than leaves, gardeners would be protected. Actually, many humans consume low dietary Zn, and increased crop Zn could be beneficial.

Stop 5/16/83

REGULATORY STRATEGIES FOR METAL CONTROL

METALS TO BE REGULATED

The USEPA (EPA, 1979a) has only regulated the application of cadmium to land in sewage sludge and other wastes. Other metals which have been identified as potentially phytotoxic or food-chain contaminants (Cd, Pb, Hg, As, Se, Zn, Cu, Ni, Mo) have not been regulated at the Federal level. Many states have considered Pb, Zn, Cu, Ni, Hg, and even Cr. Cadmium has received regulatory attention because of the relative ease with which it is taken up by crops, and because of the relatively small difference between current dietary Cd intake and the presumed safe intake level (Ryan et al., 1982).

Although there appears to be little present justification for general regulation of metals other than Zn, Cu, Ni and Pb, Chaney (1983b) lists several which should require attention in the form of further research or sludge monitoring programs. These are sludge borne metals which can escape the "Soil-Plant Barrier" (Se, Mo) or are added to soils in industrial wastes (Be, Co), or may cause animal health problems when sludge is ingested (above metals plus F and As). Regulations may be required in some instances to prevent direct ingestion of sludge or soil which has received sludge.

Many states regulate Zn, Cu, and Ni application to reduce risk of phytotoxicity.

METAL LEVELS IN SLUDGES

One regulatory approach to the control of potential problems from metals in sludges is to restrict the land application of sludges which have metal concentrations in excess of prescribed levels. This approach is relatively easy to monitor, and has the advantage of encouraging sludge pretreatment by individual POTW's. The levels of individual metals that constitute a "safe" sludge is, and has been, a topic of considerable debate. Chaney (1973), in his Conference paper, suggested that a sludge that would be appropriate for land application should not exceed the following metal concentrations:

Chaney (1973) Chaney & Giordano (1977)

	————— $\mu\text{g/g}$ dry weight —————	
Zn	2000	2500
Pb	1000	1000
Cu	800	1000
Ni	100	200
B	100	--
Hg	15	10
Cd	0.5 % of Zn	25 (1.5% of Cd)

Chaney felt that these levels were reasonably attainable. Note that, at 0.5% of the 2000 $\mu\text{g/g}$ maximum Zn concentration, the maximum Cd content would be 10 $\mu\text{g/g}$. Chaney and Giordano (1977) subsequently suggested maximum levels of metals in domestic sludge.

Doty et al. (1978) presented the following recommended maximum concentrations for Pennsylvania sludges which they attribute to Baker and Chaney (no reference given), and which are designed to allow safe annual sludge applications at a rate of 22.4 mt/ha:

µg/g dry weight	
Cd	50
C	1000
Cr	1000
Pb	1000
Hg	10
Ni	200
Zn	2000

Although these are suggested maximum concentrations, Pennsylvania does not regulate application rates on the basis of metal levels in sludges. Japan regulates maximum sludge Cd, Hg, and As levels at 5, 2, and 50 µg/g (Ishikawa and Dodo, 1982). The ranges of maximum allowable concentrations in European and Canadian sludges for As, Cd, Cr, Cu, Hg, Mo, Ni, Pb, Se and Zn are 10-75, 10-40, 200-1,200, 500-3,000, 5-25, 20-40, 100-500, 300-2,000, 14-40 and 1,850-10,000, respectively (M. D. Webber, Dept. of Environment, Burlington, Ontario, personal communication).

At the present time, metal levels in sludges are not regulated by USEPA except that sludges which contain < 2 µg Cd/g dry weight are exempt from current regulations on pH control. Many states (e.g. OH, PA, MD, VA, NY, CN) regulate maximum sludge metal concentrations.

Early in 1980, USEPA released in pre-proposal draft form rules that would constitute a comprehensive federal sludge management policy (Newkumet, 1980). The approach proposed by USEPA was to establish maximum concentrations of cadmium and lead in sludge for various end uses. Sludge fertilizers for unrestricted use would have a fixed nitrogen to cadmium ratio which would limit increases in soil Cd over a 25-year period to 0.5-2.5 µg/g. A restricted use category for sludge fertilizers (non-food chain uses) would allow a lower N:Cd ratio. Similar ratios of N:Pb would limit Pb accumulation in the top one centimeter of soil over a 25-year period to 250-1000 µg/g. Sludge products to be used as soil conditioners for unrestricted use could contain 2.5-10 µg/g Cd and 150-1000 µg/g Pb if the material also had a Cd:Zn ratio < 1.5% and contained at least 10% CaCO₃ equivalent by weight. Restricted soil conditioning sludge products could have 10-25 µg/g Cd and 250-1000 µg/g Pb.

These proposals have generated considerable discussion since they were first proposed. Although EPA has revised their draft in light of newer information, the agency has not proposed them for public comment. This approach offers significant incentives to POTW's to improve the quality of their sludges, and opens the door to more widespread sale and distribution of sludge products. On the other hand, there is some concern about the ability of large POTW's to reduce metal levels to background levels to the point where they can meet the proposed concentrations. In addition, more recent information on the dietary intake of Cd

(Ryan et al., 1982) and the risks associated with other metals should be evaluated before establishing final rules on metal concentrations in sludge products.

ANNUAL AND/OR CUMULATIVE METAL LOADINGS

The current regulatory approach in the United States and many other countries is to restrict the cumulative and annual application of metal to soil. In the U.S., Cd is the only metal that is currently regulated, but it is likely that the same approach would be appropriate for other potentially toxic metals which accumulate in soil. The W-124 (formerly NC-118) Regional Research Committee (EPA, 1980) reviewed the development of guidelines for metal loadings as follows:

1. Chumbley (1971) was one of the first to propose limiting metal accumulations in soil. He proposed a maximum accumulation of 560 kg/ha of Zn equivalent, where $\text{Zn equivalent} = \text{Zn} + 2 \text{ Cu} + 8 \text{ Ni}$. The coefficients of the equation reflect the relative phytotoxicities of the three metals.
2. Leeper (1972) suggested combining the Zn equivalent approach with CEC and proposed a maximum Zn equivalent accumulation of 5% of the CEC.
3. In 1974, USEPA published a draft technical bulletin which proposed to increase the allowable Zn equivalent to 10% of CEC and decrease the relative phytotoxicity of Ni with respect to Zn from 8 to 4. In addition, they proposed that the Cd:Zn ratio not exceed 1:100. The Cd:Zn ratio had been proposed by Chaney (1973) as a means of preventing excessive Cd uptake since Zn would become phytotoxic before Cd had accumulated to excessive levels.
4. In the same year, an NC-118 subcommittee met to review the proposed USEPA guidelines and suggested that: (1) the Zn equivalent approach implied more knowledge about the relative phytotoxicities of Zn, Cu and Ni than actually existed; (2) Cd and Pb additions to soil should also be controlled due to human health concerns; (3) the annual rate of Cd application should not exceed 2.24 kg/ha (2 pounds/acre) (based on field data from Wisconsin which showed slight increases in grain Cd at 4.48 kg/ha annual rate but not at 2.24 kg/ha); (4) the cumulative Cd application should not exceed 11.2 kg/ha. This was based on the notion that, after five years at the maximum annual application rate of 2.24 kg/ha, the accumulation would still be within the range encountered for natural mineral soils (Allaway, 1968). It was felt that, after five years, there would be further research data to give a more accurate value; (5) allowable accumulations of Pb, Ni, Zn and Cu should reflect current knowledge of their relative phytotoxicities. Based on these criteria, NC-118 suggested the following maximum accumulations for medium textured soils in the North Central region of the U.S., assuming that soil pH would be ≥ 6.5 :

	lbs/ac	kg/ha
Pb	1000	1120
Zn	500	560
Cu	250	280
Ni	100	112
Cd	10	11.2

These were intended to be lifetime accumulations.

5. In 1976, the NC-118 Committee, at the request of USDA, modified their guidelines to distinguish between fine, medium and coarse textured soils. In addition, the allowable Ni addition was increased to the same level as Cu. This resulted in the values given previously in Table 1, and which have been adopted as guidelines or regulations by many state regulatory agencies.
6. In 1978, EPA reprinted the North Central Research Publication No. 235 which included the revised Ni levels (Knezek and Miller, 1978).
7. In 1979 (EPA, 1979a) USEPA published final, interim final and proposed regulations for land application of sewage sludges. Cd was the only metal addressed, and the section of the rules (interim final) that apply to metals can be summarized as follows:
 - 1) The annual Cd application will not exceed 0.5 kg/ha for tobacco, leafy vegetables or root crops grown for human consumption.
 - 2) For other food-chain crops, the annual Cd application rate will not exceed:

	kg/ha
Present to June 30, 1984	2.0
July 1, 1984 to Dec. 31, 1986	1.25
After Jan. 1, 1987	0.5

- 3) The cumulative Cd application to soils used for the production of food-chain crops will not exceed those given in Table 9.
- 4) No maximum annual and cumulative Cd applications are specified, but the only food-chain crop produced is animal feed, the pH of the soil/sludge mixture is 6.5 wherever crops are grown, there is a facility plan which demonstrates how the animal feed will be used to preclude its ingestion by humans, and future property owners are notified that the land has

TABLE 9. MAXIMUM CUMULATIVE CD APPLICATIONS TO SOIL (EF., 1979a)

CEC (meq/100 g)	Maximum Cumulative Application (kg/ha)		
	Background pH \geq 6.5	Background* pH < 6.5	Background pH < 6.5
<5	5	5	5
5-15	10	10	5
>15	20	20	5

*Soil/sludge pH is 6.5 whenever food-chain crops are grown.

received Cd applications and should not be used for food-chain crops. (This "dedicated site" approach will be discussed later).

The phased reduction of the annual Cd application rate of 2.0 kg/ha originally proposed by NC-118 in 1974 (actually 2.0 pounds/acre) was justified by USEPA as being necessary for the long-term protection of the nation's food-chain, and the phased-in reductions would provide the necessary lead time for POTW's to develop their pretreatment programs. The CAST (1980) Report examined the existing data on effects of annual versus cumulative Cd additions on Cd uptake by various crops. They concluded that, while there was a clear positive relationship between the total amount of Cd applied and Cd uptake at a given pH, there were no clear-cut differences between annual versus cumulative additions. This follows from previous discussion in this paper which indicated that previous Cd additions did not rapidly revert to less available forms. There appears, then, to be little justification for required annual Cd application rates < 2.0 kg/ha as long as the cumulative provisions are followed. However, lower Cd sludges allow much greater sludge benefit to be applied at the desired cumulative Cd limit. British scientists conclude that the original Zn (equivalent) limitations were for extractable metals. Using extractable:total ratios for the EDTA and acetic acid extracts used in the UK, Williams (1982) indicated that British total soil metal restrictions would be similar to the NC-118/USDA values.

SOIL PH AND CEC

Soil pH

Chumbley (1971) suggested that soil pH should be >6.5 to reduce phytotoxicity of Zn, Cu and Ni. In 1974, NC-118 (USEPA, 1980) proposed that soil pH should be 6.5 at the time of sludge application and maintained at > 6.2 after application. The 1976 CAST Report recommended that soil pH be maintained at ≥ 6.5.

In the current USEPA regulations (EPA, 1979a), the soil/sludge mixture pH at the time of application must be ≥ 6.5 wherever food-chain crops are grown. The regulations provide for lower cumulative Cd limits (5 kg/ha) for soils whose background pH is < 6.5 and the soil/sludge pH will not be ≥ 6.5 at some time after sludge application. This provision is particularly important for those soils, primarily in the unglaciated regions of the eastern, southeastern and northwestern U.S., that have high lime requirements to reach pH 6.5.

Soil pH is the factor which has most consistently been shown (CAST, 1980) to affect Cd uptake of crops at a given level of Cd in the soil. Soil acidity is regularly neutralized by liming in normal farming operations, and pH 6.5 is close to the optimum for most crops and for those soil processes which lead to improved crop growth. A few crops are grown in strongly acidic soils (<5.5) to prevent plant diseases (some potato and tobacco cultivars).

CEC

The current USEPA regulations (EPA, 1979a) on cumulative Cd additions distinguish between these CEC classes: < 5, 5-15 and > 15 meq/100 g soil. The evolution of this approach has been discussed previously. The W-124 Regional

Research Committee (EPA, 1980) and the 1980 CAST Committee (many of the W-124 members also served on the CAST Committee) reviewed the existing data on the effects of CEC on Cd uptake by plants and concluded that it was difficult to establish a direct link between CEC and metal uptake because most of the studies were confounded by pH and soil organic matter content. The Committees felt, however, that CEC reflected a number of the soil properties which result in metal retention and decreased plant uptake. In addition, CEC is a routinely measured soil parameter and familiar to agriculturists. Several problems were identified, however, with the use of CEC to regulate Cd accumulation by crops: (1) on calcareous soils, Cd uptake appears to be insensitive to changes in CEC, (2) effects of CEC on uptake of other metals (e.g. Ni, Cu, Zn) may not hold for Cd, and (3) the CEC relationship may be most valid for soils with a mixture of organic matter, aluminosilicate clay minerals and Fe, Al and Mn oxides, but may not hold for soils dominated by any one of these constituents.

Future research should concentrate on the effects of soil minerals, organic matter and pH on metal uptake and regulations should be refined to reflect advances, as they occur, in our knowledge of the soil-metal system.

SLUDGE CHARACTERISTICS

The regulatory approach used in the U.S. and many other countries is to restrict metal applications to soil regardless of sludge characteristics and sludge metal bioavailability. But recent work (Corey et al., 1981) would indicate that the bioavailability of a metal can vary depending on the chemistry of the sludge, and that, in some cases, the metal-binding capacity of the sludge may be as, or more, important than soil characteristics in determining metal uptake by crops.

Research should focus on developing extraction procedures, adsorption isotherms or other methods of determining the metal retention capacity of different sludges which might, in the future, provide the means to regulate sludge-metal additions to soil on the basis of sludge as well as soil characteristics.

BACKGROUND METAL LEVELS IN SOILS

Extensive information on background levels of metals in uncontaminated soils has been developed in recent years (Allaway, 1968; Page, 1974; Baker and Chesnin 1976; Pierce et al., 1982; Logan and Miller, 1983). A survey of metal levels of uncontaminated soils in the U.S. is presently being conducted by the Soil Conservation Service (USDA-USEPA-USFDA cooperative study). These data will provide a basis for comparison with soil tests from sites which are known to have received, or are suspected of having received metal additions in the past. As land application of sludges and other wastes which contain metals increases, the need to monitor prior applications also increases, especially if there has been inadequate documentation of previous metal additions. At the present time, most of the available data is on total metal content of soil, and research indicates (CAST, 1980) that total metal content of soil gives reasonable correlations with metal uptake by crops when other factors, such as pH, are constant. In the future, however, new soil test procedures may be sufficiently accurate to measure available metal levels in soils, and provide a better indication of metal uptake than total metal content of soil.

FOOD-CHAIN VERSUS NON FOOD-CHAIN PLANTS

The current USEPA regulations are designed to prevent excessive uptake of metals by food-chain crops. These include crops ingested directly by humans such as fruits, vegetables (and includes tobacco) and grains, as well as crops which are primarily fed through livestock. Land used to grow tobacco, leafy vegetables and root crops grown for human consumption (EPA, 1979a) can receive no more than 0.5 kg/ha/yr compared to the phased reduction of the annual rate for other crops from 2 down to 0.5 kg/ha by 1987. The cumulative metal accumulations are the same for all food-chain crops, however, based on the acidic garden scenario. While there are no restrictions on the accumulation of metals in soil for growth of non food-chain species, there is an implicit understanding in the regulations that prior accumulations of metal while non food-chain species were grown would apply to food-chain crops if there was a planned land use change to crop production.

There does not appear to be any new research since the promulgation of the 1979 regulations that would indicate that they are ineffective in controlling excessive Cd uptake. Of greater concern, is the lack of monitoring of small users of sludge products (the home gardener) who is likely unaware of the metals content of the product he is using and of the health risks associated with excessive metal ingestion. This problem was considered by USEPA (Newkumet, 1980) in their proposed regulations for the sale and distribution of sludge products, and it appears that this is the only manageable approach to controlling the commercial dissemination of sludge-borne metals into the human environment.

FDA "SAFE" LIMITS

An alternative method of controlling metal uptake by the food-chain is to establish maximum concentrations of metals in crops and livestock that would be "safe." Chaney (1973) in his Conference paper raised the possibility of establishing permissible Cd contents of foods in the marketplace. The difficulties of doing this, however, are many. A "safe" limit can only be established for a particular crop or food in terms of its contribution to the total diet, the transmission of the metal from the crop or food into humans, and the existing and maximum allowable metal burden in the diet (based on full toxicological understanding). The Food and Drug Administration (FDA) has not been able to establish "safe" limits in crops and foods even for a single metal, cadmium, which has received enormous attention in recent years (Ryan et al., 1982). FDA presently has limits on Hg in fish and Pb in canned milk and baby formulas.

Even if the dietary scenarios can be established, setting a metal concentration limit in crops is difficult. Crops differ greatly in their uptake of metals, translocation of the metals from roots to shoots, and in relative transport of metals into fruits, tubers, and grains (Chaney and Hornick, 1978; Chaney, 1983b). There are also significant differences among cultivars of the same crop species (CAST, 1980).

Using the "safe" limit approach would also entail extensive crop monitoring, and it is not clear at this time how a nationwide monitoring program would be run or enforced or could be afforded. Interpretation of a crop monitoring program will require some knowledge of the background levels of metals in major crops. Presently, USDA-USEPA-FDA are conducting a nationwide survey of metals in

crops grown on uncontaminated soils. The complete data will not be available for another year or so, but some of the preliminary results have been reported for wheat (Meyer et al., 1982). These results will be invaluable in determining the variability in metal content of crops, and may help to determine if the "safe" level approach is a viable regulatory alternative.

INTENSIVE (DEDICATED SITE) VERSUS EXTENSIVE (LOW APPLICATION RATE) STRATEGIES

The 1979 USEPA regulations provide for two approaches to land application of sewage sludges (EPA, 1979a). The first approach controls the annual and cumulative Cd additions to cropland and is designed to regulate sludge applications at rates which allow for efficient crop utilization of sludge nitrogen. This is usually < 15 dry metric tons/hectare. This extensive approach will result in a slow accumulation of metals on a significant portion of agricultural land in the U.S. (Logan, 1983). As reviewed in this paper, these levels may cause no practical change in Cd in crops, at least for low Cd sludges (Chaney et al. 1983b). At crop utilization rates, 0.5-40% of the available cropland in a state may be required for land disposal of all POTW digested sludges (USDA, 1978). Critics of this approach will argue that it is potentially dangerous to allow even low level contamination of such a large percentage of our food-producing resource. On the other hand, increases in our knowledge of food-chain effects of specific metals will hopefully keep pace with the slow rate of metal addition to land with this approach. This conclusion should be tempered, however, by the realization that chronic levels of toxic metals in the human diet may take decades to exhibit recognizable disease symptoms.

The second approach proposed by USEPA (EPA, 1979a) involved higher applications of sludges to land at "closely controlled facilities." This would permit greater metal additions than in the previous approach, but management would control the disposition of food-chain crops and would monitor surface and groundwater to prevent their contamination. This approach is currently used, to various degrees, by many POTW's (Forster et al., 1981), although, in many cases, there is inadequate monitoring of crops, soil and water. This "dedicated site" approach is favored by those who feel that contamination under controlled conditions of a small part of our food-producing soil resource is less of a long-term risk than a strategy of more extensive landspreading (Logan, 1983).

Regardless of the relative merits of these two approaches, it is difficult in practice to define "dedicated site" management systems. Forster et al. (1981) surveyed Ohio POTW's and found that several had been spreading sludge on the same land for many years. In some cases this was POTW-owned land, but in other instances neighboring farmland was used. There was little indication from the survey that the 1979 USEPA regulations for "dedicated sites" was being followed.

PROCEEDINGS
TOXIC ELEMENT STUDIES
FOOD CROPS AND URBAN VEGETABLE GARDENS

A SYMPOSIUM

Sponsored by
Cornell University Cooperative Extension New York City Gardening Program
at
The Wave Hill Center for Environmental Studies
The Bronx, New York
June 14, 1978

 **COOPERATIVE
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New York City Gardening Program

program

TOXIC-ELEMENT STUDIES:
Food Crops and Urban Vegetable Gardens

A Symposium

Sponsored by the New York City Gardening Program
Albert Harris, Jr., Program Leader
at

The Wave Hill Center for Environmental Studies
Betty T. Greenfield, Executive Director

June 14, 1978

9:00 **Registration and Coffee**

9:45 **Welcome and Introduction**

Dr. Eugene M. Ezersky—Coordinator, New York City Programs, Co-operative Extension, Cornell University

Comments of Moderator

Dr. David L. Call—Director, New York State Cooperative Extension

10:00 **Minimizing Heavy-Metals Content in Crops Grown in Urban Vegetable Gardens**

Dr. Rufus L. Chaney—Plant Physiologist, Biological Waste Management and Soil Nitrogen Laboratory, U.S.D.A., Beltsville, Md.

10:30 **The Cornell Study—Lead and Cadmium in Demonstration Gardens and Market Vegetables**

Dr. Theo J. Kneip—Deputy Director, Laboratory for Environmental Studies, Institute of Environmental Medicine, New York University Medical Center

11:00 **Effects of Ingested and Inspired Lead on Body Functions of Adults and Children**

Dr. Anita Curran—Deputy Commissioner of District Health Services and Director of the Bureau of Lead Poison Control, New York City Department of Health *

11:30 **Sources of Lead and Cadmium in the Diet**

Dr. Samuel I. Shibko—Chief of Contaminants and Natural Toxicants Evaluation Branch, Division of Toxicology, F.D.A., Washington

12:00 **Box Lunch and Walk Around Grounds and Sculpture Gardens**

1:15 **Panel Discussion on Morning Talks and Related Matters**

Dr. Call moderating

3:45 **Conclusion**

Dr. Ezersky

*Since the symposium, Dr. Curran has become Westchester County's Commissioner of Health.

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REPORT ON THE NYC-UGP CABBAGE FEEDING STUDIES - 1977-78

Gilbert S. Stoewsand

Associate Professor of Toxicology
Cornell University
Department of Food Science & Technology
N. Y. S. Agricultural Experiment Station
Geneva, New York 14456

Methods & Materials: Twenty heads of cabbage, var. "Green Winter", were grown in each of the 10 NYC gardens, brought to Geneva, and processed according to the scheme of Fig. 1. Control cabbage, var. "Green Winter" was generously donated for this project by the Dick Martin Farms about 3 miles northwest of Brockport, N.Y. This cabbage was processed in an identical manner.

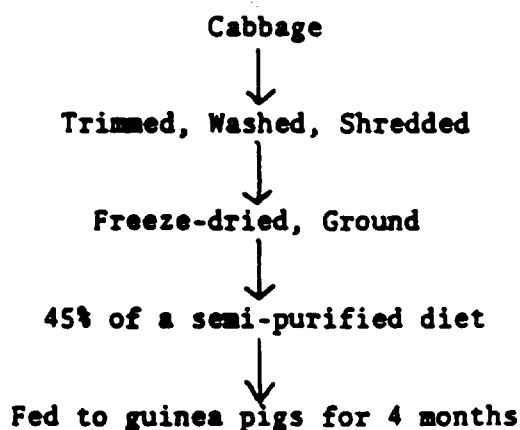
Young, male guinea pigs, Hartley strain albino, with an average initial weight of about 180 g. were purchased from a commercial supplier, and placed on one of the two 45% cabbage diets, after a week of gradual introduction to the food. Initially there were 12 guinea pigs per each of the two treatments fed in pairs within stainless steel suspended cages with diets and water supplied ad libitum. Due to a few animals unable to adapt to the treatments and loss from heart punctures when we tried to obtain blood (we later learned enough blood could be obtained by cutting their nails), only 7 NYC and 5 Brockport treated animals completed the 4-month experimental period.

The semi-purified diet was the Briggs-Williams diet, containing 28% casein, 7.5% corn oil, 1% L-arginine, and all required minerals and vitamins including an additional 0.2% ascorbic acid. The 45% freeze-dried cabbage replaced essentially all of the fiber and most of the carbohydrates, except for 7.9% sucrose, recommended for the basal diet. The calcium content was calculated at 1.23% and the Zn content was .0104g/kg of diet. The cabbage was not analyzed for these elements prior to feeding.

Blood analysis was accomplished by "Accu-Stat" modules and reagents (Clay Adams). Hepatic microsomal enzymes, *p*-Nitroanisole O-demethylase and Aminopyrine N-demethylase are routinely run in my laboratory. Increased levels of these enzymes could indicate diets containing organic foreign compounds, e.g. polyaromatic hydrocarbons, PCB's, etc.

Figure 1.

NYC-UGP Cabbage Feeding Study



Results: Table 1 shows the 4-month body weight gains and total average diet intake. The NYC cabbage group averaged lowered weight gains but the figures are not significant ($p>0.05$).

Table 2 shows the higher average liver weights and both hepatic microsomal enzymes were increased in the NYC group but was not statistically significant ($p>0.05$).

Table 3 shows the blood chemistry data. There was a significant ($p<0.05$) lowering of serum albumin in the guinea pigs fed the NYC cabbage as compared to the average level of serum albumin in the Brockport cabbage group (control). Although this level of albumin is within the normal range of guinea pigs, lowered serum albumin could mean the start of kidney damage. This damage is accompanied by a loss of albumin through the kidneys.

Tables 4 and 5 present the data of the mean cadmium and lead residues present in the liver, kidney, adrenals and spleen of the guinea pigs. Tom Greweling of the Department of Agronomy, Ithaca did the analysis by atomic absorption spectroscopy. Every tissue examined showed an increase in cadmium and lead in guinea pigs fed the NYC cabbage. Lead residues in liver and adrenals of the NYC group showed statistically significant ($p < 0.05$) increased values. NYC cabbage was approximately 100% higher in cadmium and lead as compared to the control cabbage.

The comparatively high kidney residues of cadmium in guinea pigs fed the NYC cabbage could be responsible for the observed lowered serum albumin in these animals. Cadmium is known to produce kidney damage in animals and man. Since cadmium is known to concentrate within the kidney cortex, analyzing only this portion of the organ would undoubtedly yield much higher cadmium residues. We did not separate the cortex from the medulla of the guinea pig kidneys prior to analysis.

Table 1.

Four Month Weight Gains and Diet Intake
of Guinea Pigs Fed UGP-Cabbage

<u>Cabbage*</u>	<u>Weight Gain</u> g	<u>Diet Intake</u> g
NYC (7)	322 \pm 30	2823
Brockport (5)	404 \pm 43	2962

*Green winter var.; number of animals in parenthesis.

Table 2.

Liver Weight and Hepatic Mixed Function Oxidase
Activity of Guinea Pigs Fed UGP-Cabbage

<u>Cabbage</u>	<u>Liver weight</u> ¹	<u>p-Nitroanisole</u> ² <u>O-demethylase</u>	<u>Aminopyrine</u> ² <u>N-demethylase</u>
NYC	3.4 ± 0.2	10.9 ± 1.2	14.9 ± 1.2
Brockport	3.0 ± 0.1	8.2 ± 1.4	9.9 ± 2.3

¹ as % of body weight

² nM product/mg protein/hr

Table 3.

Blood Chemistry of Guinea Pigs Fed UGP Cabbage

<u>Cabbage</u>	<u>Hb</u> <u>g %</u>	<u>Glucose</u> <u>mg %</u>	<u>Urea N</u> <u>mg %</u>	<u>Uric Acid</u> <u>mg %</u>	<u>Cholesterol</u> <u>mg %</u>
NYC	14.5 ± 0.2	125 ± 8	25.8 ± 1.2	6.5 ± 1.6	58.3 ± 4.2
Brockport	15.0 ± 0.1	133 ± 5	28.2 ± 1.4	6.1 ± 0.6	55.8 ± 2.0

	<u>Total Protein</u> <u>g %</u>	<u>Albumin</u> <u>mg %</u>	<u>Alk. Ptase.</u> <u>Bu</u>	<u>SGOT</u> <u>Ku</u>	<u>SGPT</u> <u>Iu</u>
NYC	6.30 ± 0.14	3.48* ± .09	35.2 ± 1.9	45.5 ± 12	75.2 ± 7
Brockport	6.32 ± 0.12	3.80 ± .04	42.4 ± 5.2	40.2 ± 9	93.2 ± 9

* Significant lower (P<0.05)

Table 4.

Mean Cadmium Residue in Organs¹ of Guinea Pigs Fed UGP-Cabbage² Diets

Liver		Kidney		Adrenal		Spleen	
Brockport	NYC	Brockport	NYC	Brockport	NYC	Brockport	NYC
6.4±.8	9.2±1.7	26.6±3.7	44.3±7.8	0.2±.04	0.3±.07	2.2±.4	4.3±.8

¹ mcg/g of dried tissue² Brockport = 0.51 ppm Cd

NYC = 0.97 ppm Cd

Table 5.

Mean Lead Residues in Organs¹ of Guinea Pigs Fed UGP-Cabbage² Diets

Liver		Kidney		Adrenal		Spleen	
Brockport	NYC	Brockport	NYC	Brockport	NYC	Brockport	NYC
0.96±.04	1.46±.14 ³	1.7±.6	2.9±.2	0.54±.18	1.46±.23 ³	2.8±.3	2.9±1.0

¹ mc/g of dried tissue² Brockport = 2.2 ppm Pb

NYC = 5.3 ppm Pb

³ Significantly increased (P<0.05)

Recommendation: It is recognized the problems and pitfalls involved in predicting human hazards from laboratory animal studies. From a rather short-term period, with few animals fed an accentuated cabbage diet we are trying to establish dietary hazards of individuals over a 70 year lifetime. Therefore, rather cautious, conservative recommendations should be forthcoming from any study of this type. If we err we should err on the conservative side.

The animal studies indicate a warning signal. Cadmium and lead are increased in the tissues of guinea pigs fed NYC cabbage. A slight, but significant serum albumin lowering in these animals may be indicative of an initial adverse physiological response of animals fed this vegetable. In addition, laboratory animals exhibiting cadmium residues in their kidneys to the level of the NYC cabbage fed guinea pigs in this study have developed hypertension.

From these results and since any increase in dietary lead and cadmium in the diets of people, especially children, should be avoided it is my recommendation that NYC cabbage, as well as other leafy vegetables grown on the UGP should not be consumed. Unless cultural practices, such as liming or other means of changing soil pH, could reduce heavy metal uptake, these vegetables that are known to be heavy metal accumulators should be eliminated from the NYC-UGP, as well as in other inner city vegetable garden programs.

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Sources and Levels of Lead and Cadmium in the Diet

by

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Sources and Levels of Lead and Cadmium in the Diet

For non-industrially exposed individuals food may represent the major source of exposure to lead and cadmium, although exposure to lead from air and water is also significant. Therefore, it is important to trace some of the routes by which these toxic elements enter the food supply.

Essentially 3 sources contribute to the presence of lead in food. First, there is the so-called natural background level. This background is present because the ubiquitous distribution of lead in the environment (soil and water) which results in its being incorporated into all living organisms, although it has not been established that lead is an essential nutrient for any organism. The remainder of the lead in food is present as a result of two aspects of man's activities: these can be subdivided into (a) pollution of the environment with lead and (b) food processing activities involving the use of lead. In environmental pollution, lead dust fallout from automobile exhaust or lead smelting operations or lead in runoff water from mining operations may cause additional lead to enter food and feed crops in limited geographical areas. The use of lead pesticides may also increase levels of lead in certain fruits and vegetables, and in addition, where the use of such pesticides has been long established, increased levels of lead in the soil may cause further increases of lead in such crops. Automobile exhaust may be an important source of additional lead in crops grown in urban gardens, either because the levels of lead in soil increase, particularly in areas near busy roadways, or because

heavy lead dust settles on plants and is difficult to remove completely by washing, since some of the material may become tightly bound or embedded in the waxy cuticle of the plant. Foliar absorption of lead has not been established. It appears that little, if any, aerosol-deposited lead is actually taken up through plant leaves. However, the deposition of lead on plant surfaces cannot be ignored as a potential hazard either from ingestion of garden produce directly by man, or from entry into the food chain when the plants are fed to cattle.

Household dusts containing high levels of lead that settle on prepared foods may also represent another source of lead. House dust samples taken in New York and Boston in the early '70s contained 0.1 to 0.2% of lead by weight; 100 mg of this dust would contain 100 ug of lead, an amount approximately equivalent to that in the whole adult diet for one day. At present, there is no definitive information on how much additional lead is ingested from these sources.

The most important source of additional lead in the food supply from food processing is the method of packaging and holding food. Foremost among these sources of added lead is the popular "sanitary" or tin can, which is used to package 10-15 percent of all food. Thirty-three billion tin cans are used each year to package food and approximately another 25 billion are used annually to package carbonated beverages. The source of added lead from tin cans is not the can itself, but the lead solder. It is estimated that about 20% of the lead in the average daily diet of persons older than 1 year is from canned food, of which about 2/3 is

from the solder, the remainder is in the food itself prior to canning.

Other incidental and rather minor added sources of lead include migration of lead from ceramic glazes, silver plated holloware, porcelain pots and pans, pewter and fine leaded crystal under normal conditions of use. However, misuse of glazed ceramic ware by storage of acid foods or drinks for prolonged periods can result in the leaching of significant amounts of lead into the food. Drinking water, and hence water used to prepare foods, also contains very low levels of lead. The maximum permissible level for lead in drinking water is 50 ug/L but this level may be exceeded in some communities. Although in some communities the problem of elevated lead levels in water is associated with the use of lead plumbing in soft water areas and can be corrected by adjusting the pH of the water, other areas appear to have naturally high background levels of lead in water. Extremely minor sources of lead are contributed to food by the presence of unavoidable low levels of lead present in some food additives and colors. The levels of lead and other heavy metals in food additives and colors are limited by specifications for acceptable food ingredients such as those published in the Food Chemicals Codex.

Cadmium, like lead, has an extremely generalized distribution. It is present in all food groups. Cadmium can be incorporated into foods from a variety of sources. However, the prime source, which results in the so-called 'natural background level', is the ubiquitous distribution of cadmium in the environment, although it has not been established to be an essential nutrient for any organism. A number of

additional factors (man-made or natural) may also contribute to the levels of cadmium in the food supply. As with lead, the chief route by which cadmium enters food is through crops and animal feed.

Cadmium is scarcely ever found except as a contaminant of zinc minerals in the earth's crust at a Cd/Zn ratio of approximately 1/350 in such minerals as zinc blende and calamine, and at a ratio of approximately 1/160 in soil. The amount of cadmium absorbed by plant roots depends on the availability of the cadmium in the rock or soil. There is no information on the form in which cadmium is translocated in the plant. Cadmium, like other heavy metals, is not readily translocated in plants. In grasses and cereals (rice) and in other plants, the highest concentration of cadmium is present in the roots; lower concentrations are found in the stem and grain. In general, data are lacking on the translocation of cadmium in other plants, although certain leafy vegetables show relatively high levels of cadmium when grown on cadmium-containing soils. Cadmium uptake by plants is related to zinc uptake, although some plants may show a preferential uptake of cadmium over zinc. Other characteristics of cadmium uptake by plants include the presence of cations from other sources that compete for exchange sites on the soil, and soil pH. Man's activities may contribute significantly to the potential for increased levels of cadmium in food in addition to the normal background levels. Smelters and refineries, particularly those involved in zinc and copper operations, are major sources of cadmium pollution, and so, to a lesser extent, are city incinerators that burn refuse containing cadmium pigments. Major contamination of vegetation from these sources

is limited to areas in the vicinity of the industrial plant or incinerator. The concentration of cadmium in the soil varies inversely with the distance from the point source (smelter or incinerator). Lands that were very infrequently tilled, e.g., areas of grass and alfalfa cultivation, showed a maximum buildup of cadmium and other metals studies, whereas gardens and fields of wheat, barley and oats that were tilled yearly showed the lowest concentration. The cadmium content of vegetables grown within the polluted area varied directly with the amount of metal in the soil. Measurement of cadmium in dustfall in various parts of the United States indicates that in urban areas, over 2 g cadmium per acre is deposited yearly and in rural areas about 1 g/acre/year (normal application of fertilizer to pasture land would add about 1 g cadmium/acre/year). These low levels would not be expected to cause significant contamination of soil or bodies of water.

Another source of cadmium pollution may be motor vehicles, as recent studies have indicated that roadside soil is contaminated by cadmium. The concentrations of cadmium, nickel, lead, and zinc in soil and vegetables were shown to decrease with the distance from the road, indicating their relation to the amount of traffic. The cadmium appears to be derived from oils and motor vehicle tires. Other routes by which cadmium is introduced into plants relate directly to agricultural practices. Vegetation grown in fields irrigated with cadmium-contaminated water shows high levels of cadmium. Runoff from mine tailings or from electroplating washing processes may contribute to the problem in limited areas. The use of superphosphate fertilizers containing relatively high cadmium levels has been suggested as an important factor contributing to the level of cadmium in crops. Sewage sludges containing

high levels of cadmium also represent a significant potential route for entry of cadmium into crops. The cadmium in such sludges is derived primarily from the electroplating industry. The normal background levels of cadmium encountered in animal tissues are presumably derived from cadmium in animal feed or pasture. Tissue levels are normally low, although high values have been observed for kidneys, but increase with the age of the animal. The presence of cadmium in the aquatic environment is of concern because of the ability of aquatic organisms to concentrate trace contaminants, with the possibility of a food chain accumulation of the element. Studies of fresh water fish suggest the unlikelihood of any marked food chain accumulations of the element, and the high levels of cadmium observed in fish are due to direct concentration from sea water. The highest cadmium concentrations are observed in shellfish, which have a marked ability to accumulate cadmium (as well as other transition metals) in the viscera. In general, food processing does not appear to increase the level of cadmium in food. The use of cadmium in ceramic glazes represents a very minor source of exposure to cadmium under normal conditions of use.

The source of lead and cadmium are summarized on slide 1.

Because oral ingestion of lead and cadmium via foods may represent one of the most important source of intake of these metals, it is important to have accurate information on levels of exposure from this source. It is particularly important to have information on normal background levels of these elements in the diet, so that estimates can be made of any additional exposure, to lead and cadmium from the use of home-grown vegetables as substitutes for commercially available vegetables. From these data, some evaluation can be made of possible health hazards. As other speakers have discussed, our concern about effects of lead and cadmium, on health is chiefly related to long-term, low dose exposure to these elements, rather than the occasional high level exposure. In other words, duration of exposure to increased levels of either lead or cadmium, is as important as the actual increase in level.

Much of the basic data on levels of lead and cadmium in the food supply and estimates of exposure to these elements from the diet have been obtained from the continuing Market Basket Program of the National Pesticides Monitoring Program of the FDA, and since 1973, a new FDA program called Heavy Metals in Foods. In the market basket program, foods are purchased according to a specified list of 117 items. Contents and portions are prepared to simulate the diet of a 16 to

19-year-old male, statistically the nation's largest eater. The food is divided into 12 categories and composites of each category are prepared and analyzed. The levels of lead and cadmium in the composites from the 1974 survey, listed in slide 3, show that on a national basis lead and cadmium were present in all composites from all food groups. The relative contributions of the various classes of food to dietary lead and cadmium are shown in slides 4 and 5. About 16% of the total lead in the diet, and about 30% of the cadmium are contributed by vegetables and fruits that might reasonably be expected to be grown in urban gardens. However, studies of the Market Basket type, in which foods are analyzed in composite categories rather than individually, run the risk that unusually high metal concentrations may be masked when the foods are combined into composites with other foods that typically have much lower metal contents, e.g., cadmium when meats and poultry are composited with fish. The Heavy Metals in Food survey, on the other hand, is designed to measure the content of lead, cadmium and zinc in individual foods rather than in composites. Foods covered in the survey were selected by the following criteria: (1) relative importance

in the diet, both adult and infant, (2) past indication of particularly high levels of the metals in the selected foods, and (3) balanced coverage of raw and processed foods. The next series of slides (SLIDES 6, 7, 8 and 9) summarizes average values and ranges of lead and cadmium in some food surveyed. Adult foods and baby foods, are grouped separately.

In the survey of adult foods, the mean level was highest in canned tomatoes, with canned beans, canned peas and canned peaches next in order. Milk and sugar had the lowest mean levels. Overall, 96% of the samples contained less than 1 ppm lead, 80% less than 0.5 ppm, and 35% had no detectable levels of Pb. In the case of infant foods, orange juice had the highest mean level; apple juice, applesauce and peaches, vegetables and beef, and vegetables had the lowest lead levels. In adult foods, cadmium is generally present in meats more often and in high concentration than in other foods. Concentrations in grain and cereal items are also higher than in other foods. Overall, 99% of the adult samples contained 0.1 ppm cadmium or less, 61% contained .01 ppm or less, and 35% had no detectable cadmium. In general, the baby foods surveyed contained very low levels of cadmium.

Slide 10 provides an overview of the extent to which canning may be a source of increased levels of lead and cadmium in foods. Lead levels are clearly increased by the canning process, but cadmium levels do not appear to be increased. These results have been confirmed by comparing levels of lead and cadmium in canned foods with those in glass-packed foods and raw agricultural produce.

The FDA has initiated several programs to reduce lead in the food supply, particularly food items intended for young infants. For example, when sampling of evaporated milk, disclosed excessive levels of lead, FDA initiated a quality assurance program with industry to assure compliance with a 0.5 ppm limit. The average lead level in canned milk has since declined from 0.52 ppm to 0.1 ppm at present. Evaporated milk before canning contains 0.05 ppm lead. Lead levels in canned infant fruit juices have been reduced from an average of 0.3 ppm in 1973 to 0.05 ppm today. In addition, industry had achieved a significant reduction in lead content of glass-packed foods through careful product selection and preparation. A cooperative effort of canners and can makers has reduced the lead level in canned foods. In addition, another program recently commenced by the USDA and FDA relates to levels of lead and cadmium in raw agricultural produce. Some data from these studies are shown in slide 11.

It is important to recognize that the levels of lead and cadmium in the diet represent average values of exposure. There is some regional variation, as is shown in the last slide. In addition, the levels of metals in foods are highly variable, and for the most part uncontrollable. However, the available data permit us to compare estimated average intakes of these metals with what are considered to be tolerable levels. This approach is probably valid because the long biological half-life of metals in the human body makes it more important to consider intake over a long period of time, than to stress the importance of occasional high intakes of the elements. In order to determine if any possible health problem is related to the use of urban-grown vegetables, it will be necessary to obtain detailed data not only on levels of lead and cadmium in the crops, but on the amount and frequency with which they are consumed, to determine if (a) they contribute significantly to the total exposure to these elements, and (b) their use results in exposure to elevated levels of these elements for significant periods of time.

SLIDE I

Sources of Pb and Cd in Food		
	Pb	Cd
Natural Background	Soil, Water	Soil, Water
Agricultural	Lead Arsenate Pesticides	Phosphate Fertilizers Sewage Sludge Cd as contaminant in Zn Pesticides Irrigation Water
Environmental Contamination	Pb in air (automobile exhaust) Mining and Smelting Operations	Cd in air from automobile tires Incinerators Mining and Smelting Operations
Minor Sources	Ceramic Glazes Porcelain Pots Pewter Food Chemicals and Colors Leaded Crystal	Ceramic Glazes Porcelain Pots
Food Processing	Tin Cans	

SLIDE 2

FY 74 RELATIVE COMPOSITION OF DIET BY FOOD CLASS

	<u>Food Group</u>	<u>Avg. g/Day</u>	<u>% of Total Diet</u>
I.	Dairy	763	25.7
II.	Meat, Fish, and Poultry	267	9.0
III.	Grains and Cereals	422	14.2
IV.	Potatoes	183	6.2
V.	Leafy Vegetables	55	1.8
VI.	Legume Vegetables	69	2.3
VII.	Root Vegetables	33	1.1
VIII.	Garden Fruits	92	3.1
IX.	Fruits	221	7.4
X.	Oils and Fats	72	2.4
XI.	Sugars and Adjuncts	82	2.8
XII.	Beverages (including water)	712	24.0
	Total	2971	100.0

SLIDE 3

Mean Lead Contents of Food Groups and Their Contribution to Daily Lead Intake (Adults)*

Food Group	Conc ppm Mean	Intake ug/day	Percent of Total Daily Diet	Contribution to Daily Lead Intake	
Dairy	0.02	15	25.9	8.2	
Meat, Fish and Poultry	0.14	37	9.9	20.0	
Grains and Cereals	0.08	33	12.6	18	
Potatoes	0.05	9	7.0	4)	
Leafy Vegetables	0.13	7	2.0	4)	
Legume Vegetables	0.11	7	2.5	4)	17.4%
Root Vegetables	0.15	5	1.2	2.7)	
Garden Fruits	0.05	5	3.0	2.7)	
Fruits	0.10	22	1.8	12.1	
Oils and Fats	0.05	4	2.8	2.2	
Sugar and Adjuncts	0.02	2	23.9	1.1	
Beverages	0.05	36	20	20	

*Source - U. S. DHEW/FDA FY 74, Heavy Metals in Foods Survey

SLIDE 4

Mean Cadmium Contents of Food Groups and Their Contribution to Daily Cadmium Intake (Adults)*

Food Group	Conc ppm Mean	Intake ug/day	Percent of Total Daily Diet	Contribution to Daily Cadmium Intake	
Dairy	0.005	3.94	25.9	7.7	
Meat, Fish and Poultry	0.0093	2.49	9.9	4.9	
Grains and Cereals	0.028	11.66	12.6	22.8	
Potatoes	0.046	9.11	7.0	17.8)
Leafy Vegetables	0.051	3.18	2.0	6.2)
Legume Vegetables	0.006	0.42	2.5	0.8) 29.7%
Root Vegetables	0.021	0.76	1.2	1.5)
Garden Fruits	0.019	1.71	3.0	3.4)
Oils and Fats	0.027	1.36	1.8	2.7	
Sugar and Adjuncts	0.0083	0.68	2.8	1.3	
Beverages	0.0057	6.49	23.9	12.7	

*Source - U. S. DHEW/FDA FY 74, Heavy Metals in Foods Survey

SLIDE 5

Mean Lead Contents of Food Groups and Their Contribution to Daily Lead Intake*
(Toddlers - 2 Yrs Old)

Food Group	Total Wt Consumed (g/day)	Conc ppm Mean	Intake ug/day	Percent of Total Daily Diet	Contribution to Daily Lead Intake
Whole Milk	508	.05	25	32.6	24.6
Other Dairy & Substitutes	68	.02	1.76	4.3	4.2
Meat, Fish and Poultry	126	.14	17.64	8.1	8.0
Grain and Cereal Products	116	.08	9.2	7.4	7.3
Potatoes	35	.05	1.75	2.2	1.72)
Vegetables	73	.11	8.03	4.6	4.5)
Fruits & Fruit Juices	145	.10	14.5	9.3	14.28
Oils and Fats	15	.05	.75	0.9	.73
Sugar and Adjuncts	30	.03	.9	1.9	.85
Beverages (Including Drinking Water)	439	.05	22	28.23	27.8

*Source - U. S. DHEW/FDA FY 74, Heavy Metals in Foods Survey

SLIDE 6

CONTENT OF LEAD IN SELECTED ADULT FOODS*

Commodity	No. of Samples	Average ppm	Standard Deviation ppm	Range, ppm	
				Low	High
Carrots, roots fresh	70	.205	.517	0	3.54
Lettuce, raw crisp head	69	.130	.292	0	2.02
Potatoes, raw white	71	.050	.101	0	0.762
Butter	71	.068	.195	0	1.51
Margarine	71	.048	.056	0	.37
Eggs, whole fresh	71	.174	.310	0	4.02
Chicken fryer, raw					
whole or whole cut up	71	.127	.191	0	1.30
Bacon, cured raw, sliced	71	.099	.251	0	1.685
Frankfurters	69	.198	.446	0	2.87
Liver, raw beef	71	.089	.150	0	1.03
Hamburger, raw ground beef	71	.248	.578	0	8.29
Roast, chuck beef	71	.071	.120	0	0.54
Wheat flour, white	71	.052	.175	0	1.62
Sugar refined, beet or cane	71	.031	.058	0	0.44
Bread, white	70	.084	.132	0	0.91
Orange juice, canned frozen					
concentrate	71	.135	.612	0	5.2
Green beans, canned	71	.318	.273	0	1.34
Beans, canned with pork and					
tomato sauce	71	.638	.665	0	4.74
Peas, canned	71	.425	.747	0	6.95
Tomatoes, canned	71	.710	.838	0	4.81
Diluted fruit drinks, canned	71	.251	.446	0	3.18
Peaches, canned	71	.417	.342	0	2.908
Pineapple, canned	71	.402	.455	0	7.10
Applesauce, canned	71	.320	.291	0	3.03

*Source - U. S. DHEW/FDA FY 74, Heavy Metals in Foods Survey

SLIDE 7

Lead Contents of Selected Baby Foods*

Commodity	No. of Samples	Average ppm	Standard Deviation ppm	Range, ppm	
				Low	High
Vegetables and beef	71	.070	.088	0	.67
Mixed vegetables	71	.072	.168	0	1.12
Spinach	69	.085	.093	0	.55
Orange juice	71	.375	.583	0	3.66
Apple juice	71	.321	.284	0	1.47
Applesauce	71	.160	.195	0	1.37
Pears	71	.079	.067	0	.494
Peaches	71	.094	.083	0	.458
Apricots	71	.082	.101	0	.63

*Source - U. S. DHEW/FDA FY 74, Heavy Metals in Foods Survey

SLIDE 8

Cadmium Content of Selected Adult Foods*

Commodity	No. of Samples	Average ppm	Standard Deviation ppm	Range, ppm	
				Low	High
Carrots, roots fresh	69	0.051	0.077	0	0.70
Lettuce, raw crisp head	69	0.062	0.124	0	1.06
Potatoes, raw white	71	0.057	0.139	0	0.36
Butter	71	0.032	0.071	0	0.68
Margarine	71	0.027	0.048	0	0.50
Eggs, whole fresh	71	0.067	0.072	0	1.48
Chicken fryer, raw whole or whole cut up	71	0.039	0.088	0	0.82
Bacon, cured raw, sliced	71	0.040	0.160	0	1.55
Frankfurters	69	0.042	0.111	0	0.65
Liver, raw beef	71	0.183	0.228	0	1.24
Hamburger, raw ground beef	71	0.075	0.122	0	2.56
Roast, chuck beef	71	0.035	0.034	0	0.63
Wheat flour, white	71	0.064	0.150	0	1.48
Sugar refined, beet or cane	71	0.100	0.709	0	6.16
Bread, white	70	0.036	0.063	0	0.439
Orange juice, canned frozen concentrate	71	0.029	0.095	0	0.883
Green beans, canned	71	0.018	0.072	0	0.49
Beans, canned with pork and tomato sauce	71	0.009	0.000	0	0.068
Peas, canned	71	0.042	0.113	0	0.118
Tomatoes, canned	71	0.042	0.113	0	0.87
Diluted fruit drinks, canned	71	0.017	0.052	0	0.37
Peaches, canned	71	0.036	0.061	0	0.95
Pineapple, canned	71	0.059	0.153	0	0.99
Applesauce, canned	71	0.020	0.027	0	0.195

*Source - U. S. DHEW/FDA FY 74, Heavy Metals in Foods Survey

SLIDE 9

Cadmium Content of Selected Baby Foods*

Commodity	No. of Samples	Average ppm	Standard Deviation ppm	Range, ppm	
				Low	High
Vegetables and beef	71	0.026	0.035	0	0.24
Mixed vegetables	71	0.034	0.052	0	0.401
Spinach	69	0.057	0.054	0	0.43
Orange juice	71	0.040	0.084	0	0.43
Apple juice	71	0.023	0.035	0	0.264
Applesauce	71	0.007	0.023	0	0.18
Pears	71	0.013	0.053	0	0.520
Peaches	71	0.003	0.005	0	0.04
Apricots	71	0.011	0.037	0	0.32

*Source - U. S. DHEW/FDA FY 74, Heavy Metals in Foods Survey

SLIDE 10

Mean Levels of Metals in Foods
Surveyed in FY 74 Heavy Metals Program

	<u>Mean PPM</u>	
	<u>Lead</u>	<u>Cadmium</u>
All Adult Foods (32)	0.246	0.047
Canned Adult Foods (13)	0.376	0.029
Non-Canned Adult Foods (19)	0.156	0.060
Baby Foods (9)	0.149	0.024

SLIDE 11

Vegetable	No. of Samples	LEAD (ppm)		CADMIUM (ppm)		ZINC (ppm)	
		AV	RANGE	AV	RANGE	AV	RANGE
White Potatoes	48	0.02 - 0.19	ND - 0.61	0.01 - 0.03	ND - 0.07	2.4 - 5.4	1.4 - 6.3
Lettuce	37	0.01 - 0.04	ND - 0.2	0.01 - 0.03	ND - 0.11	0.9 - 1.9	T - 2.9
Dry Onions	48	0.01 - 0.04	ND - 0.27	0.0 - 0.01	ND - 0.10	0.3 - 3.0	T - 46
Cabbage	46	0.01 - 0.06	T - 0.18	0.0 - 0.03	ND - 0.08	1.4 - 2.4	ND - 4.6
Tomatoes	46	0.03 - 0.22	ND - 0.53	0.01 - 0.02	ND - 0.07	1.1 - 11.4	ND - 24.3
Sweet Corn	48	0.06 - 0.23	ND - 1.0	0.0 - 0.06	ND - 0.50	6.5 - 10.4	T - 10.7
Green Peas	50	0.03 - 0.08	ND - 0.13	0.0 - 0.08	ND - 0.08	10.2 - 11.1	7.2 - 13.6
Snap Beans	27	0.0 - 0.07	ND - 0.42	0.0 - 0.02	ND - T	2.7 - 23.3	1.5 - 29.0
Carrots	48	0.0 - 0.12	ND - 0.62	0.01 - 0.07	ND - 0.08	2.3 - 3.4	1.4 - 5.0

HEAVY METALS IN CROPS (USDA/FDA Survey, 1977)

(Areas involved include Wisconsin, California, Florida, Texas, Indiana, Michigan, Illinois, Ohio, Louisiana, Iowa, Missouri, Minnesota, Washington, Maryland)

184
70
06
36
68
50
48
82
55
55
4
56
63
48
16
439
883
149
068
118
87
37
95
79
95

SLIDE 12

Geographic Variations of Toxic Elements in Food*

<u>Geographic Region</u>	<u>FY 74 Samples</u>	<u>ug/day Lead</u>	<u>ug/day Cadmium</u>	<u>ug/day As₂O₃</u>	<u>ug/day Selenium</u>	<u>ug/day Mercury</u>
NE	10	105.5	32.1	31.3	146.9	2.39
SE	7	75.7	24.1	11.4	154.1	3.84
C	6	105.5	35.5	4.4	197.8	3.59
<u>W</u>	<u>7</u>	<u>69.7</u>	<u>43.3</u>	<u>28.6</u>	<u>190.5</u>	<u>1.85</u>
Total U.S.	30					
Average Residue Levels		90.2	33.5	20.7	168.9	2.84

Baltimore District	= SE
Boston District	= NE
Minneapolis District	= C
Kansas City District	= C
Los Angeles District	= W

*Source - U. D. DHEW/FDA FY 74, Heavy Metals in Foods Survey

CONCENTRATIONS OF LEAD AND CADMIUM
IN GARDEN VEGETABLES GROWN IN NEW YORK CITY

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INTRODUCTION

Current studies of the effects of toxic elements emphasize the use of modern instruments and vastly expanded knowledge of physiology and biochemistry to search for effects at exposures previously considered normal. However, despite these efforts our knowledge remains limited regarding the sources of low level or "normal" exposures.

In considering the presence of toxic elements in food, these questions regarding the sources are of major concern. The concentrations in soil used for vegetable growing are the first consideration, but dustfall and soldered cans have also been reported as significant sources. For instance, the work of the Bureau of Foods of the Food and Drug Administration (1) has shown an average contamination due to the canning of adult food of about 0.2 μg Pb/g food (wet basis). The FDA study indicates that the food industry has reduced the level of lead in processed baby foods; however, concern exists about the margin of safety in lead exposures of the very young child (2).

A number of studies have been reported on the determination of the route of uptake of either or both lead and cadmium by food crops. Most recently Chaney (3) has reported

the multiple factors involved in the uptake of cadmium from soil. These include cadmium and zinc concentrations and soil pH and cation exchange capacity as major factors. Under adverse conditions, substantial uptake can occur and proteinaceous fractions of the food crop can become high in cadmium. A review has been published on lead in vegetation by Zimdahl and Koeppe (4). While similar soil factors may be involved in uptake of lead, the transfer occurs less readily, and formation of an insoluble lead phosphate in the outer root layers is believed to limit translocation within the plant. Various studies have demonstrated contamination due to airborne lead, but the confounding effect of soil lead and the problem of differentiating exterior from absorbed contamination have left the quantitative details in question.

In studies aimed at relating health effects to geochemical variations Warren, et al. (5) found lead concentrations in English garden vegetables ranging from 5 to 300 $\mu\text{g Pb/g ash}$. The vegetables included root, legume, leafy and head types. These values were found for gardens with soil lead concentrations of 36 to 960 $\mu\text{g Pb/g soil}$ (as extracted with sulfuric acid). Soils of much lower lead contents were analyzed, but vegetable samples were not obtained. Warren and others found a relation of various soil trace element patterns to disease incidence, but could not demonstrate exposure of the populations through food intake. The data is not provided for conversion of ash

weight to wet weight basis, but division by a factor of from fifty to one hundred would be appropriate. In a subsequent study (6) Warren and Delavault reported a range of 0.2-2.3 μg Pb/g dry basis in cabbages, 0.2 to 7.6 in potatoes, 0.2-11 in carrots, 1-12 in beans, and 0.3 to 56 $\mu\text{g/g}$ for lettuce. Loss on drying values reported in this study could be used to convert these values to wet basis. Both Underwood (7) and Mahaffey (2,8) have recently reviewed the multiple sources of lead exposure.

The FDA has estimated population exposures of cadmium (1) for the U.S., and Underwood (7) has reviewed the literature reports. While estimates of total dietary intakes are quite variable, concentrations in fruits and vegetables are believed to be below 0.1 μg Cd/g wet weight. Both fertilizers and airborne contamination are suspected to contribute to the presence of cadmium in foods. No contamination was observed due to the canning process (1).

The available data indicates very large variations in toxic element concentrations within a given food crop. Studies of potential effects of specific sources must therefore be designed to establish not only concentrations for such a source, but also concentrations in alternate sources for comparison.

A preliminary study was initiated through the cooperative efforts of the Council on the Environment and the Cooperative Extension of Cornell University in 1976. The data indicated

that garden crops from New York had lead concentrations in the ranges reported by the FDA, but might fall on the elevated side of national means. In 1977 the Cooperative Extension Program of Cornell University sampled and analyzed garden crops and soils from the Urban Garden program initiated that year. Market crops were also analyzed to obtain data on trace element concentrations from that source.

EXPERIMENTAL

Samples of individual crops were taken at each of 10 garden sites (2 per Borough) in New York City during July and August of 1977. The fresh vegetables were washed thoroughly with tap water, root crops were peeled, and each sample was weighed, labeled, placed in a plastic bag and frozen on the day of sampling. The frozen samples were transported to the Ithaca campus where they were freeze dried, ashed, dissolved and analyzed by atomic absorption spectrophotometry (9). The site locations are given with soil and traffic data in Table I.

In order to provide for representative sampling, two gardens were chosen from each borough, and several soil types were represented. One-half of the soils were the original soil present at the location, four were topsoil brought in (two from Long Island and two from Staten Island) and one was from a garden long established on landfill material. Long-established, well supervised programs existed at the Botanical Gardens, and other sites represented a range of new to already organized community garden projects.

No effort has been made to cover gardens of individuals. This first study is designed to evaluate the potential risks in large scale, well organized and supervised community gardening programs such as that being carried out by the Cornell Cooperative Extension with support from the U.S. Department of Agriculture.

RESULTS

The vegetable portion of the U.S. diet has been characterized by the FDA in categories of leafy greens, legumes, roots and garden fruits. These categories are adopted here for purposes of comparison (and for use in calculation of changes in dietary exposures).

The results given in Table II are reported on a wet weight basis together with average moisture content data. Conversions of dry weight to wet weight values have been made accurately with individual sample moisture and analytical data, but the average moisture values could generally provide sufficient accuracy for such conversions.

The samples of leafy greens from the gardens were principally cabbage and collard greens as lettuce was not available during the sampling in July and August, while cabbage and lettuce were obtained from the markets. The market lettuce was low in lead compared to the other crops, but several samples had elevated cadmium. Market cabbage was about one-fourth as high in lead as the garden samples.

While no differences are apparent for the legumes, the sampling is insufficient to represent even the gardens

studied. No clear cut conclusions can be drawn for the crop as yet. The root crops, principally carrots and turnips, are generally elevated in lead compared to the market vegetables which were two-thirds carrot samples. All garden fruit samples, both market and New York garden sources, gave uniformly low values for lead and cadmium. The leafy vegetables which contain more lead when urban grown, present the most likely source of a hazard.

If only Manhattan and Brooklyn are taken into account, the results used represent the highest lead contaminations as only these boroughs exceed the city average. (One sample at 1.69 $\mu\text{g Pb/g}$ is excluded as being an inedible portion of the collard plant sampled.) The values in Table III show the averages as calculated for Manhattan and Brooklyn combined.

The results of the New York study are compared in Table IV to data for the national FDA sampling of 1974. Several clear conclusions can be drawn from this comparison. In general the ranges for the New York samples are smaller, and means tend to be closer to median values indicating more homogeneity than that present in the nationwide sampling.

The cadmium concentrations in all New York samples are about the same as those found in the national study. Where average differences do occur they are small, and the upper limits of the values for New York are well within the upper limits for the national samples.

Garden vegetables have higher concentrations of lead than national or market samples in the case of leafy greens

and root crops, but both New York sources are lower for the garden fruits. It is probable that the canned samples used by the FDA for garden fruit samples (tomatoes) and legumes (green beans and peas) account for the apparently elevated lead levels in those samples.

DISCUSSION

Atmospheric lead concentrations have been decreasing in New York City since the early 1970's. The concentration of lead in gasoline was regulated by the city in 1970 and airborne concentrations have declined at rooftop levels in mid-Manhattan from 2-3 $\mu\text{g}/\text{m}^3$ to less than 1 $\mu\text{g}/\text{m}^3$ from 1969 to 1976. Nevertheless, street level concentrations at specific locations may still be relatively high, and soil lead has been accumulated from years of fallout.

Neither airborne nor soil cadmium would be expected to be unusually high in New York, as no major industrial sources exist in the city. Aerosol concentrations are generally below 10 ng/m^3 . However, the gardens studied were found to have variable concentrations of cadmium and zinc in soil, and variable soil pH levels as well (see Table V).

PLANT UPTAKE

Reduced metal uptake is reported for increased soil pH, increased available calcium (for Pb), increased available Zn (for Cd), increased cation exchange capacity, increased organic matter, increased phosphate (for Pb) and decreased available lead and cadmium concentrations. This is an

extremely complex series of interactions and many contradictory findings have been reported due to uncontrolled variables in experimental designs.

Uptake of lead is believed to be most significant through the roots with foliar uptake minimal (4). Airborne lead can, however, be held on leaf surfaces and extremely careful washing has been necessary to avoid confusion in the results of experimental studies.

Cadmium is more readily taken up from soils, the concentration in plants showing an inverse relation to the soil pH (3). The FDA has recommended that the application for sewage sludge on land be limited to a maximum of 9 lbs. of cadmium per acre and 900 lbs. of lead per acre for a soil of 5-15 in cation exchange capacity (10). These values would be about 100 μg Cd/g soil and 8,000 μg Pb/g soil at a soil density 1. The New York garden soils do not contain these metals in nearly the amounts allowed for sludge amendment.

The available data do not indicate that either soil or airborne lead values in New York City should be of consequence in contamination of crops grown in New York. Evaluation of the garden crop data has resulted in no evidence to support a relation between lead in leafy vegetables or root vegetables and either soil lead or soil pH (Figure 1). Airborne lead data are not available at these locations for comparisons. Further studies must be undertaken to widen the scope of soil sampling based on preliminary data from Boston (11).

For cadmium both soil pH and Zn/Cd ratio appear to have an effect. Plots of average concentrations in plants versus soil values for each garden show the relations for leafy greens as seen in Figure 2. The data indicate that increased soil pH and Zn/Cd may cause decreased cadmium uptake in root and leafy vegetables in agreement of the controlled studies previously discussed.

Root crops show only 2.3 fold average increase in lead compared to market crops, while leafy greens show a 4.4 fold increase for the same comparison. In the absence of the many reported studies we could conclude that leafy vegetables simply take up more lead. However, the reports indicate that roots immobilize lead by precipitating lead phosphate and that foliage should be 100 times lower than roots and grain 100 times than foliage (4). While these comparisons were not made across species, the general trends could be expected to hold. In view of reported difficulty in washing produce free of lead in other research studies, it appears that lead in both leafy greens and legume crops may be in part due to deposition from the air.

CONCLUSIONS

These results provide assurance that the levels of cadmium in vegetables from New York's urban gardens are low and do not present a hazard in comparison to other sources of vegetables. Careful observance of soil pH controls should lead to still lower levels for some gardens. The values for lead, while somewhat elevated for certain crops,

are within the range of national samples and do not appear to present a serious hazard.

An estimate of the lead hazard from the garden vegetable source will be made in a subsequent paper through application of diet composition data reported in various national nutritional studies.

ACKNOWLEDGEMENT

The data on garden and market crop trace element concentrations were compiled in a sampling and analysis program performed under the direction of Professor Donald Lisk of Cornell University. Dr. Thomas Greweling of Cornell University directed the analytical work. My thanks to them and to the New York City Garden Program personnel, especially Al Harris, Herley Thompson, Sharon Kahkonen, and the garden supervisors who helped in the sampling. The gardeners themselves cooperated by sacrificing their crops to make the work possible.

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TABLE I
DEMONSTRATION GARDENS 1977
NYC Gardening Program

<u>BOROUGH</u>	<u>SOIL TYPE</u>	<u>SOURCE</u>	<u>TRAFFIC</u>
<u>Bronx</u>			
182nd Street (at Washington Ave.)	Clay loam	Long Island Top Soil	Moderate
Botanical Garden (Southern Blvd. at 185th St.)	Clay loam (Landfill)	Landfill (a)	Heavy 200 yds.
<u>Manhattan</u>			
12th St. (between Aves. A and B)	Clay loam	Long Island Top Soil	Light to moderate
The Farm (Grand & Suffolk)	Clay loam	Staten Island Top Soil	Moderate to heavy
<u>Queens</u>			
Rochdale (N.Y. Blvd. between 137th Ave. & Bedell St.)	Sandy loam	Original	Light
Botanical Garden (Main St. & College Pt. Blvd.)	Clay loam	Original	Moderate
<u>Staten Island</u>			
Snug Harbor (Richmond Terrace)	Clay loam	Original	Light
Miller Field (New Dorp Lane)	Clay loam	Original	Light

TABLE I (continued)

<u>BOROUGH</u>	<u>SOIL TYPE</u>	<u>SOURCE</u>	<u>TRAFFIC</u>
<u>Brooklyn</u>			
Baltic Street (600 Baltic St. between 4th & 5th Ave.)	Clay loam	Staten Island Top Soil	Moderate
Brooklyn College Children's Garden (Campus Rd. between E. 21 & E. 22nd St.)	Clay loam	Original	Light

(a) 70 to 80-year old land fill, local soils used at that time.

TABLE II
AVERAGE LEAD AND CADMIUM CONTENT BY CROP AND LOCATION

Leafy Greens

	<u>Pb, $\mu\text{g/g}$ (wet wt) (a)</u>						<u>Cd, $\mu\text{g/g}$ (wet wt)</u>			
	<u>Garden</u>	(n)	(% < LD)	<u>Market</u>	(n)	(% < LD)	<u>Garden</u>	(n)	<u>Market</u>	(n)
New York City Mean	0.62	(16)	(89.8)	0.14	(13)	(93.8)	0.04	(16)	0.07	(13)
New York City Median	0.485			0.125			0.04		0.03	
Bronx				0.145	(3)				0.015	(2)
182nd Street	0.34	(3)					0.045	(3)		
Botanical Gardens	0.41	(1)					0.04	(1)		
Brooklyn				0.12	(3)				0.04	(3)
Baltic Street	1.69	(1)					0.07	(1)		
Brooklyn College	-			-			-		-	
Brooklyn Children's Garden	0.86	(1)					0.06	(1)		
Manhattan				0.20	(4)				0.08	(4)
The Farm	1.08	(1)					0.03	(1)		
12th Street	0.76	(3)					0.03	(3)		
Queens				0.085	(2)				0.18	(2)
Rochdale	0.59	(1)					0.04	(1)		
Botanical Gardens	0.34	(2)					0.025	(2)		
Richmond				0.12	(2)				0.01	(2)
Snug Harbor	0.35	(1)					0.05	(1)		
Miller Field	0.49	(1)					0.06	(1)		

TABLE II (continued)

Legumes (Green and Yellow Beans)^(b)

	<u>Pb, $\mu\text{g/g}$</u>			<u>Cd, $\mu\text{g/g}$</u>		
	<u>Garden</u>	(n)	(% < LD)	<u>Market</u>	(n)	(% < LD)
New York City Mean	0.24	(4)	(89.0)	0.17	(4)	(90.1)
New York City Median	0.022			0.017		
<u>Root Crops</u>						
New York City Mean	0.42	(13)	(89.6)	0.18	(9)	(86.7)
New York City Median	0.40			0.045		
Bronx	0.52	(3)				
182nd Street	-					
Botanical Gardens	0.52	(3)				
Brooklyn				0.20	(3)	
Baltic Street	0.64	(2)				
Brooklyn College	-					
Children's Garden	0.42	(1)				
Manhattan				0.13	(3)	
The Farm	0.33	(1)				
12th Street	0.41	(1)				
Queens				0.20	(2)	
Rochdale	0.30	(2)				
Botanical Gardens	0.21	(1)				
Richmond				0.24	(1)	
Snug Harbor	0.28	(1)				
Miller Field	0.42	(1)				

TABLE II (continued)

Garden Fruits^(c)

	<u>Pb, µg/g (wet wt)</u>						<u>Cd, µg/g (wet wt)</u>			
	<u>Garden</u>	(n)	(% < LD)	<u>Market</u>	(n)	(% < LD)	<u>Garden</u>	(n)	<u>Market</u>	(n)
New York City Mean	0.12	(27)	(97.4)	0.11	(20)	(94.0)	0.02	(27)	0.027	(20)
New York City Median	0.105			0.10-0.11			0.015		0.025	
Bronx				0.145	(2)				0.025	(2)
182nd Street	0.13	(3)					0.02	(3)		
Botanical Gardens	0.14	(1)					0.01	(1)		
Brooklyn				0.09	(4)				0.04	(4)
Baltic Street	0.18	(3)					0.01	(3)		
Brooklyn College	0.06	(1)					0.01	(1)		
Children's Garden	0.11	(2)					0.02	(2)		
Manhattan				0.085	(6)				0.015	(6)
The Farm	0.20	(3)					0.02	(3)		
12th Street	0.12	(2)					0.01	(2)		
Queens				0.14	(4)				0.04	(4)
Rochdale	0.08	(4)					0.02	(4)		
Botanical Gardens	0.12	(3)					0.05	(3)		
Richmond				0.10	(4)				0.02	(4)
Snug Harbor	0.09	(3)					0.01	(3)		
Miller Field	0.08	(2)					0.04	(2)		

(a) % < LD is given as loss on drying by the freeze dry method.

(b) No division is given by location as the data is insufficient for such detailed consideration.

(c) Garden fruits include tomatoes, squash, peppers, cucumbers, eggplant, etc.

TABLE III
AVERAGE LEAD IN MANHATTAN AND BROOKLYN SAMPLES COMBINED

	<u>Pb, ug/g</u>	
	<u>Garden</u>	<u>Market</u>
Leafy Greens	0.84	0.17
Legumes*	0.24	0.17
Root Crops	0.39	0.16
Garden Fruits	0.15	0.09

*Same data as for city average - samples for Brooklyn only.

TABLE IV

LEAD AND CADMIUM IN FOODS FROM NATIONAL AND NEW YORK CITY SAMPLES

	Lead, $\mu\text{g/g}$		
	<u>FDA - '74</u>	<u>NYC Market - '77</u>	<u>NYC Gardens - '77</u>
<u>Leafy Greens</u> (a)			
Median	0.001-0.09	0.12	0.48
Mean	0.13	0.14	0.62
Range	0-2.02	0.056-0.33	0.12-1.69
<u>Legumes</u> (b)			
Median	0.2-0.29	0.17	0.22
Mean	0.32	0.17	0.24
Range	0-1.34	0.15-0.19	0.22-0.28
<u>Root Crops</u> (c)			
Median	0.001-0.09 (0.2-0.29)	0.20	0.40
Mean	0.20	0.18	0.42
Range	0-3.54	0.11-0.26	0.21-1.04
<u>Garden Fruits</u> (d)			
Median	0.4-0.49	0.105	0.105
Mean	0.71	0.11	0.12
Range	0-4.81	0.05-0.17	0.04-0.29

TABLE IV (continued)

	Cadmium, $\mu\text{g/g}$		
	<u>FDA - '74</u>	<u>NYC Market - '77</u>	<u>NYC Gardens - '77</u>
<u>Leafy Greens</u> (a)			
Median	~ 0.03	0.03	0.04
Mean	0.062	0.07	0.04
Range	0-1.06	0.001-0.20	0.01-0.07
<u>Legumes</u> (b)			
Median	<< 0.01	0.025	0.02
Mean	0.018	0.02	0.02
Range	0-0.49	0.09-0.28	0.01-0.03
<u>Root Crops</u> (c)			
Median	~ 0.01	0.035	0.045
Mean	0.051	0.07	0.05
Range	0-0.7	0.02-0.28	0.07-0.13
<u>Garden Fruits</u> (d)			
Median	0.01-0.02	0.025	0.015
Mean	0.042	0.027	0.020
Range	0-0.87	0.01-0.06	0.01-0.08

(a) FDA lettuce only.

(b) Green beans in all three samples - FDA - canned only.

(c) FDA carrots only.

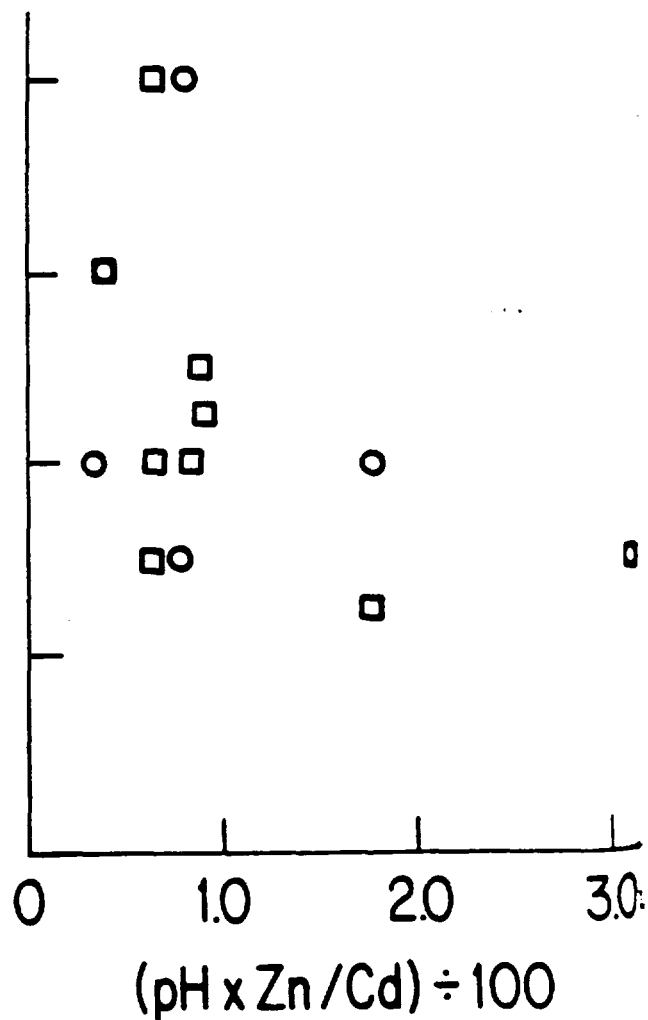
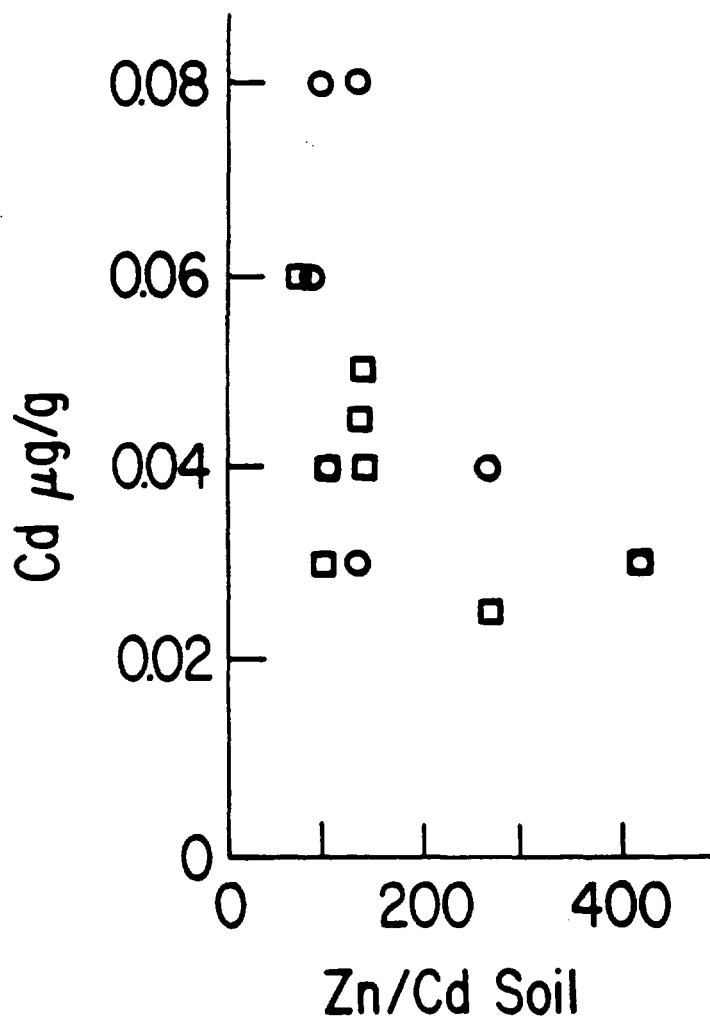
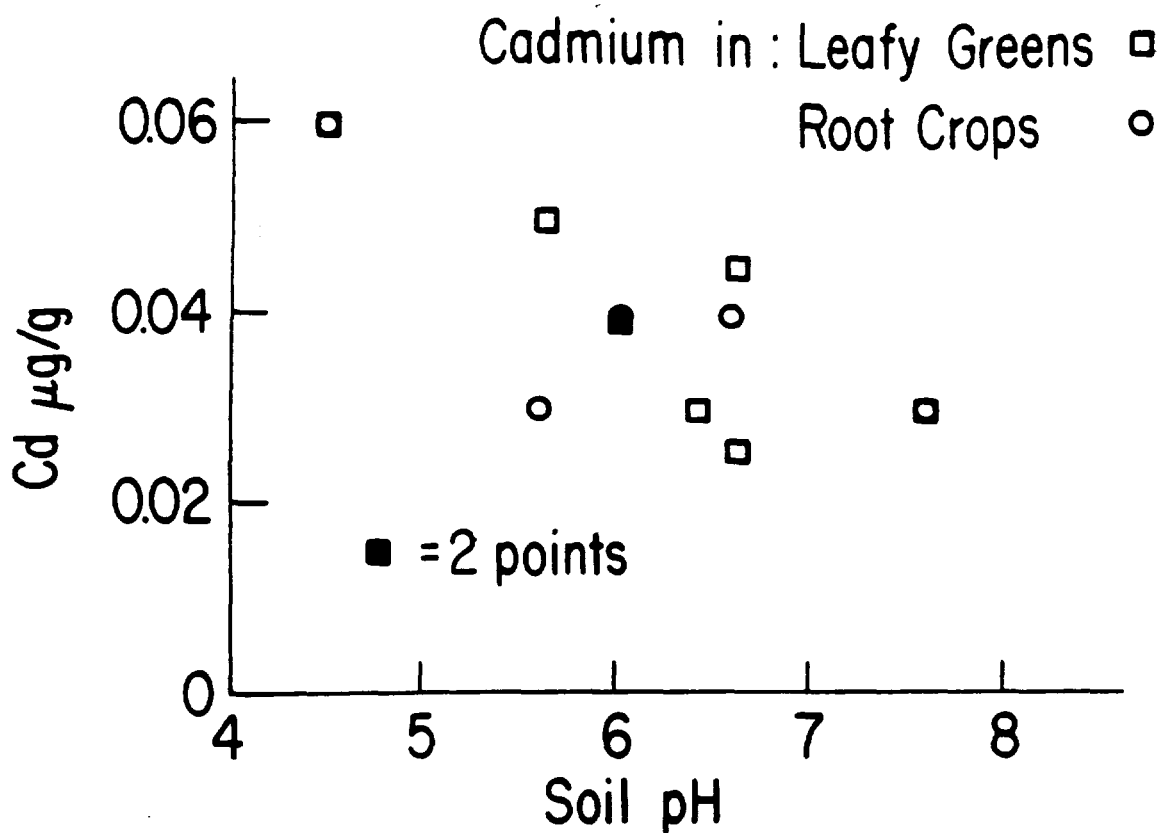
(d) FDA canned tomatoes; Market tomatoes, cucumbers, peppers;
Gardens - tomatoes, cucumbers, peppers, eggplant, squash.

TABLE V

SOIL DATA

<u>Borough Garden (a)</u>	<u>Metal $\mu\text{g/g}$ Soil</u>		<u>Soil pH</u>
	<u>Pb</u>	<u>Cd</u>	
Bronx			
182nd Street	79	0.4	6.6
Botanical Gardens	121	0.8	6.0
Manhattan			
12th Street	65	0.5	6.4
The Farm	290	0.7	7.6
Queens			
Rochdale	50	0.4	6.0
Botanical Gardens	55	0.9	6.6
Richmond			
Snug Harbor	484	0.9	5.6
Miller Field	103	0.6	4.5

(a) Brooklyn samples lost in transit.



-22-
Lead in Vegetable Crop

